Modélisation numérique des équilibres de phases et sa contribution à la compréhension des processus orogéniques

Pavel Pitra

Numerical modelling of phase equilibria and its contribution to understanding orogenic processes

Modélisation numérique des équilibres de phases et sa contribution à la compréhension des processus orogéniques

Mémoire présenté en vue d'obtenir
l'**Habilitation à diriger des recherches**
par

Pavel PITRA

Université Rennes 1
Géosciences Rennes, UMR CNRS 6118
Spécialité : Sciences de la Terre

Soutenance prévue le 17 juin 2011, devant le jury composé de

Michel BALLÈVRE, professeur, Université Rennes 1, examinateur
Jean-Pierre BURG, professeur, ETH Zürich, rapporteur
Jean-Marc LARDEAUX, professeur, Université de Nice, rapporteur
Francisco MARTÍNEZ, professeur, Universitat Autònoma de Barcelona, rapporteur
Roger POWELL, professeur, University of Melbourne, examinateur
Jean VAN DEN DRIESSCHE, professeur, Université Rennes 1, examinateur

AVANT-PROPOS

Ce mémoire écrit afin d'obtenir l'Habilitation à Diriger des Recherches à l'Université de Rennes 1 dresse le bilan de mes activités de recherche effectuées au laboratoire *Géosciences Rennes* de l'Université de Rennes 1 depuis mon recrutement comme Maître de Conférences en 1999.

Il propose d'abord un curriculum vitae qui résume aussi mes activités de recherche et de formation, complétées par une liste de mes publications et communications.

Mon approche scientifique et mes activités de recherche sont ensuite détaillées, autour du thème principal de la compréhension des processus orogéniques à travers l'étude pétrologique impliquant la modélisation numérique des équilibres de phases. Les développements futurs de l'activité de recherche que je souhaite mener sont ensuite présentés succinctement, en partie au travers de certains des projets INSU / ANR auxquels j'émarge.

Une sélection des publications récentes auxquelles j'ai participé est présentée en annexes.

TABLE DES MATIERES

A – Curriculum vitæ

ETAT CIVIL

Pavel PITRA

43 ans ; né le 31 mars 1968 à Prague (Tchécoslovaquie) ;

marié, 4 enfants (7 ; 5 ; 2 ; 0,2 ans)

Grade : **maître de conférences**

Etablissement : Géosciences Rennes – UMR CNRS 6118,
Université Rennes 1, Campus de Beaulieu,
35 042 Rennes CEDEX
Tél. : 02.23.23.65.06
E-mail : pavel.pitra@univ-rennes1.fr

NUMEN : 14S9905289CVG

DISCIPLINE DE RECHERCHE

géologie, pétrologie métamorphique

TITRES UNIVERSITAIRES ET DEROULEMENT DE CARRIERE

1999-… **maître de conférences**, depuis le 1/09/1999 ; titularisé le 1/09/2001 ; spécialité: pétrologie métamorphique

1998-99 **Chercheur post-doctoral** au Département de géologie de l'Université de Pretoria (Afrique du Sud)

1997 **Assistant de Recherche** au Département de Minéralogie, Géochimie et Ressources Minières, Universita Karlova, Prague (République Tchèque)

1992-96 **Thèse de doctorat** du Muséum National d'Histoire Naturelle (cotutelle avec Université de Prague) soutenue le 19 novembre 1996 à Paris :

"Étude pétrostructurale des régions marginales du Moldanubien de Bohême et de ses relations avec le bloc du Barrandien" ; directeurs : M. Guiraud, J-P. Burg, K. Schulmann

Jury : Jacques Fabriès, Jean-Pierre Burg, Jean-Robert Kiénast, Michel Guiraud, Karel Schulmann, Angelika Kalt.

Mention **très honorable avec félicitations**

1991-92 **D.E.A**. à l'Université de Montpellier soutenu le 8 Juillet 1992. Directeur : J-P. Burg. Mention **bien** (classement 3/28)

1986-91 4 années d'études combinées à la Faculté de Sciences et à la Faculté de Lettres de l'Université de Prague. Orientation : Géologie + Français + Russe

ACTIVITES D'ENSEIGNEMENT

Université Rennes 1 : Service supérieur à 192 heures éq. TD (194-220 h).

L2 - minéralogie, cristallographie et optique cristalline (filières " ST " et " SVT " – CM, TD, TP)
L3 - pétrologie magmatique et métamorphique (filières " ST " et " SVT " – CM, TD, TP, sorties de terrain – Bretagne)
- thermodynamique (CM, TD)
M1 - pétrologie métamorphique (filières " recherche " et " enseignement " – CM, TD, TP, stages de terrain – Alpes, Bretagne, Corse)
- encadrement des sujets bibliographiques personnels (TER) et stages professionnels
M2 - thermodynamique des roches et fluides métamorphiques (CM)

Université Bretagne Sud (Vannes) : chargé d'enseignement – pétrologie métamorphique et magmatique (CM, TP, TD ; 10-40 h en fonction des autres enseignants ; à partir de 2005)

Université de Prague et Universitat Autonòma de Barcelona – enseignement régulier dans le cadre des échanges européens **Erasmus / Socrates** - Pétrologie et équilibres de phases, cours et TD niveau master, doctorat (depuis 2002, une semaine par an)

ACTIVITES ADMINISTRATIVES

Responsabilités collectives

- Responsable des relations internationales
- Membre élu du conseil d'unité (UMR Géosciences Rennes)
- Responsable d'entretien du parc des microscopes du Laboratoire (recherche et enseignement)
- Membre de la commission " Valorisation " au sein de Géosciences Rennes
- Membre des jurys de diplôme : licence (L3), master 1 et master 2
- Responsabilité d'UE :
  - L2 : UE Matériaux géologiques (L2 PCSTM)
  - M1 : UE Magmatisme et métamorphisme (M1-ST jusqu'à 2008)
  - M2 : UE Roches et fluides métamorphiques (M2-GG)

Activité éditoriale

Rapporteur (« reviewer ») régulier pour différents journaux internationaux – ca. 30 rapports depuis 2000.

ENCADREMENT DES ETUDIANTS

Doctorat d'Université

Benjamin LE BAYON, co-encadrée à 50% avec Michel Ballèvre : *Evolution structurale et métamorphique d'une croûte continentale subductée (Grand Paradis, Alpes occidentales)* ; soutenu en 2005 ; Benjamin est actuellement en poste au BRGM

Kristina BURIANKOVÁ co-encadrée à 30% avec Jan Kosler (Prague / Bergen) : *Dating movements and metamorphism in the MCT Zone of the eastern and central Himalaya: implications for diachronous uplift of the High Himalayan rocks*. Kristina prépare sa thèse tout en travaillant à temps plein (CDI) comme chercheuse au Service Géologique Tchèque.

Martin RACEK co-encadré à 50% avec Pavla Stípská (Prague / Strasbourg). Thèse en cotutelle : *Relation of extrusion and horizontal flow of lower crust to the origin of the lower crustal wedge along eastern margin of the Bohemian massif*, soutenu en septembre 2007, actuellement en poste au Service géologique Tchèque

Abdelkhaleq AFIRI co-encadrée à 50% avec Frédéric Gueydan (40%) et Abderrahim Essaifi (10%, Univ. Marrakech) : *Etude pétro-structurale de péridotites de Beni Bousera (Maroc) et de leur enveloppe métamorphique*, soutenance prévue en 2011

Alicia LOPEZ CARMONA co-encadré à 50% avec Jacobo Abati (Madrid). Thèse en cotutelle : *Initiation de la subduction Varisque: Modélisation pétrologique et géochronologique des litholoiges de haute pression de Malpica-Tuy (Galice, NW du Massif Ibérique)* , soutenance prévue en 2012

Diplôme d'Etudes Approfondies / Master 2

Benjamin LE BAYON : co-encadré à 70% avec Pierre Gautier et Michel Ballèvre : *Le métamorphisme inverse et le développement séquentiel d'une zone de chevauchement (Marvejols, Massif Central)* ; soutenu en 2002 – classement 1er/15

Vladimir ANTONOFF : j'ai assuré la totalité de l'encadrement : *Étude des niveaux peralumineux de l'île d'Yeu (Vendée). Estimation des conditions P/T de la formation de la chaîne Varisque dans le Massif Armoricain* ; soutenu en 2005 – classement 4e/15 ; actuellement en thèse à l'Institut National de la Recherche Scientifique (Québec)

Pierre-Alban DONGUY : co-encadré à 50% avec Marc Poujol : *Dater la déformation varisque : étude pétrologique et géochronologique des zones de cisaillement métasomatiques (Ile d'Yeu, Massif armoricain)*. 2007/08. Pierre-Alban est actuellement géologue à la carrière de talc à Luzenac.

Caroline BOLLINGER: co-encadré à 30% avec Pavla Stipska et Karel Schulmann (Univ. Strasbourg): *Evolution pétrologique et analyse pression-température-déformation des éclogites de subduction du massif de Bohême* . 2008/09. Caroline est actuellement en thèse à l'Université de Lille.

Jean-Charles POILVET: co-encadré à 30% avec Marc Poujol et Jean Van Den Driessche : *Datation et mise en place des migmatites et granites C/S de la Montagne Noire*. 2009/10. J-C est actuellement en thèse à l'Université de Besançon.

Lorraine TUAL: *Evolutions progrades et rétrogrades de différentes unités métamorphiques de haute pression des Cyclades – implications pour les processus de subduction et d'exhumation*. 2010/11. J'assure la totalité de l'encadrement.

Encadrements d'autres stages

2008: **stage** de L3, Lorraine TUAL, 3 mois, Métamorphisme inverse dans la vallée du Lot

2009: **stage** de M1, Lorraine TUAL, 3 mois, Pétrologie des schistes bleus de Syros

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PARTICIPATION AUX JURYS DE DOCTORAT

- Martin RACEK (2007, Univ. Prague)	co-directeur
- Jan FRANEK (2007, Univ. Prague)	rapporteur
- Monika KOSULICOVA (2007, Univ. Strasbourg)	rapporteur
- Jirí SLÁMA (2008, Univ. Prague)	examinateur
- Ruben DIEZ FERNANDEZ (2010, Univ. Salamanca)	examinateur suppléant

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PARTICIPATION AUX PROGRAMMES DE RECHERCHE

- coordonnateur du **projet blanc INSU** (Actions sur projets INSU - Appels d'offres 2009) : **Transferts de matière et cristallisations métamorphiques : exemple du métasomatisme magnésien** (avec Philippe Boulvais, Rennes ; Didier Marquer et Philippe Goncalves, Besançon)
- **projet bilatéral PAI Picasso** entre l'Université de Rennes et l'Université de Barcelone (avec J. Van Den Driessche, F. Martínez, J. Reche) 2006 et 2007
- participation au **projet ANR** « Laterally-forced overturns (**LFO**) enhanced by melt induced softening (MIS) in orogens: new model for continental tectonics » (coordonné par K. Schulmann, Univ. Strasbourg) 2006-2009
- participation au **projet Franco-Indien: IFCPAR project n° 2307-1:** Accretionary processes of juvenile crust and continental growth: the late Archean eastern Dharwar Craton. Animateur: J-J. Peucat (Univ. Rennes 1) 2002-04
- collaboration avec l'Université de Prague sur le programme " Dating movements and metamorphism in the MCT Zone of the eastern and central Himalaya: implications for diachronous uplift of the High Himalayan rocks ", financé par la " **Grant Agency of the Czech Republic** " : thèse de K. Burianková

SEJOURS DANS DES LARORATOIRES ETRANGERS

2008 – 6 semaines à l'Université de Melbourne, Australie

RAPPORTS DE LECTURE (" REVIEWS ")

Je produis régulièrement, depuis 2000, des rapports de lecture pour de nombreux journaux internationaux – entre autres : Journal of Metamorphic Geology, Journal of Petrology, International Journal of Earth Science, Lithos, European Journal of Mineralogy, Canadian Journal of Earth Sciences, Mineralogy and Petrology, Contributions to Mineralogy and Petrology.

2006 – 4 reviews ; 2007 – 5 reviews ; 2008 – 6 reviews ; 2009 – 7 reviews ; 2010 – 7 reviews

PUBLICATIONS

Publications soumises

Gueydan, F., A. Afiri, **P. Pitra**, A. Essaifi. Oligo-Miocene exhumation of the Beni-Bousera peridotite through a lithosphere-scale extensional shear zone, Geodinamica Acta, in press.

Poilvet J-C., M. Poujol, **P. Pitra**, J. Van Den Driessche, J-L. Paquette. The Montalet granite, Montagne Noire, France: An early Permian syn-extensional pluton as evidenced by new U-Th-Pb data on zircon and monazite, Comptes Rendus Geoscience, in press.

Chopin, F., K. Schulmann, P. Štípská, J.E. Martelat, **P. Pitra**, O. Lexa, & B. Petri. Microstructural and petrological evolution of a high pressure felsic orthogneiss during continental subduction (Orlica-Śnieżnik dome, NE Bohemian Massif), Journal of Metamorphic Geology, soumis.

Štípská, P., F. Chopin, E. Skrzypek, K. Schulmann, O. Lexa, **P. Pitra**, J.E. Martelat, C. Bollinger. The role of large-scale folding on juxtaposition of eclogite and mid-crustal rocks (Orlica-Śnieżnik Dome, Bohemian Massif), Journal of Metamorphic Geology, soumis.

Articles publiés

12) **Pitra, P**., Ballèvre, M., Ruffet, G., 2010. Inverted metamorphic field gradient towards a Variscan suture zone (Champtoceaux Complex, Armorican Massif, France). Journal of Metamorphic Geology, 28, 183-208.

11) **Pitra P**., Kouamelan A. N., Ballèvre M., Peucat J. J., 2010. Palaeoproterozoic high-pressure granulite overprint of the Archaean continental crust: evidence for homogeneous crustal thickening (Man Rise, Ivory Coast), Journal of Metamorphic Geology, 28, 41-58.

10) Ballèvre, M., Bosse, V., Ducassou, C. & **Pitra, P**., 2009. Palaeozoic history of the Armorican Massif: Models for the tectonic evolution of the suture zones. Comptes Rendus Geoscience, **341**, 174-201.

9) **Pitra, P**., Boulvais, P., Antonoff, V. & Diot, H. 2008. Wagnerite in a cordierite-gedrite gneiss: witness of long-term fluid-rock interaction in the continental crust (Ile d'Yeu, Armorican Massif, France), American Mineralogist, 93, 315-326.

8) Le Bayon, B., **Pitra, P**., Ballèvre, M. & Bohn, M. 2006. Reconstructing P-T paths during continental collision using multi-stage garnets (Gran Paradiso nappe, Western Alps). Journal of Metamorphic Geology, 24, 477-496.

7) Stípská, P., **Pitra, P**. & Powell, R., 2006. Separate or shared metamorphic histories of eclogites and surrounding rocks? An example from the Bohemian Massif. Journal of Metamorphic Geology, 24(3), 219-240.

6) Racek, M., Stípská, P., **Pitra, P**., Schulmann, K. & Lexa, O., 2006. Metamorphic record of burial and exhumation of orogenic lower and middle crust: new tectonothermal model for the Drosendorf window, Bohemian Massif. Mineralogy and Petrology, 86, 221–251.

5) Ballèvre, M., **Pitra, P**. and Bohn, M., 2003. Lawsonite growth in the epidote blueschists from the Ile de Groix (Armorican Massif, France): a potential geobarometer. Journal of Metamorphic Geology, 21, 723-735.

4) **Pitra, P**. & de Waal, S. A., 2001. High-temperature low-pressure metamorphism and development of prograde symplectites, Marble Hall Fragment, Bushveld Complex, South Africa. Journal of Metamorphic Geology, 19(3), 311-325.

3) **Pitra, P**., Burg, J. P. & Guiraud, M., 1999. Late-Variscan strike-slip tectonics between the Teplá-Barrandian and Moldanubian terranes (Czech Bohemian Massif): petrostructural evidence. Journal of the Geological Society, London, 156, 1003-1020.

2) **Pitra, P**. & Guiraud, M., 1996. Probable anticlockwise P-T evolution in extending crust: Hlinsko region, Bohemian Massif. Journal of Metamorphic Geology, 14, 49-60.

1) **Pitra, P**., Burg, J. P., Schulmann, K. & Ledru, P., 1994. Late orogenic extension in the Bohemian Massif: petrostructural evidence in the Hlinsko region. Geodinamica Acta, 7(1), 15-30.

Bibliométrie

12 articles publiés ; indice de citation : 198 ; nombre moyen de citations : 16.5 ; indice H : 9

(Source : ISI Web of Knowledge, avril 2011)

environ 30 présentation dans des conférences nationales et internationales (liste non fournie)

Conférences invitées

Prague 2005, 2006
Barcelona 2008

B – Numerical Modelling of Phase Equilibria

INTRODUCTION

The aim of my scientific work is to contribute to the understanding of *geodynamic processes* using a parallel study of metamorphic processes and geological structures, while taking into account the associated magmatic and sedimentary aspects in selected key regions. The focus is on the study of pressure–temperature conditions and their evolution with time. I approach these problems from a thermodynamic point of view, through *numerical modelling of phase relations* using various types of phase diagrams calculated with the THERMOCALC software. Nevertheless, I pay particular attention to a solid field work, a sound structural investigation, and a meticulous petrographical analysis, which are essential prerequisites for the quality of the subsequent phase diagram modelling.

My publication record is not particularly rich. Yet, my contribution is significant in all papers that I co-authored and most of these papers show a citation record that is moderate but steady through the time. I tend to believe that this reflects the quality of the work.

Nor can I boast about any significant methodological developments, although this is what generally helps to boost one's citation index and what is then expected from a researcher in the current climate. Clearly, the focus of my research is the *application* of modern petrological methods to various regions in order to understand their tectonic history. I consider it as a bonus, if some sort of generally valid conclusion can be drawn from this work. My philosophy is that it would be of little use to produce models and sophisticated tools if there was nobody capable to use these tools with ability or test the models in the nature. Nevertheless, working on an interesting but local object (e.g. shear zones on Ile d'Yeu), may reveal new questions of general interest and lead to formulating new challenging projects (e.g. the development of the magnesian metasomatism). Finally, testing the models and the tools on specific field examples can show their strengths and shortcomings and possibly lead to their improvement. This is the important contribution of this kind of work to the collective effort of the scientific community to enhance our understanding of the Natural system we are living in.

The general link between most subjects approached in my research is the application of a detailed petrographical analysis of the relations between deformation and metamorphic crystallisations, and the interpretation of the observations using calculated phase diagrams. The goal is to understand the record of the *continental collision* by metamorphic rocks, from their subduction to the exhumation. The following list gives the principal problems and regions that I worked on since my arrival to the University of Rennes.

- high pressure metamorphism and subduction zones
  - the role of lawsonite (collaboration with M. Ballèvre; *publication 5*)
  - associations of rocks with contrasting metamorphic histories (Bohemian Massif; collaboration with P. Stípská; *publication 7 + submitted*)
  - PT evolution of a polymetamorphic continental crust (Alps ; PhD of B. Le Bayon ; *publication 8*)
  - initial stages of the Variscan orogeny, subduction of the Rheic ocean (blueschists in Galicia; PhD of Alicia López)
  - contrasting record of the burial and exhumation in a subduction zone (Cycladic blueschists; PhD of Melody Philippon)

- development and exhumation of inverted metamorphic sequences
  - Massif Armoricain (*publication 12*)
  - Himalaya in Nepal (PhD of K. Buriánková)
- metamorphism and tectonics of a "hot" continental crust – high pressure granulites
  - formation of high pressure granulites through homogeneous crustal thickening (Côte d'Ivoire, collaboration with Alain Kouamelan, *publication 11*)
  - burial and exhumation of orogenic lower and middle crust (Bohemian Massif – PhD of M. Racek; *publication 6 ;* project ANR – LFO)
- unravelling PT conditions of continental collision from metasomatic shear zones (Massif Armoricain – MSc of V. Antonoff – *publication 9 ;* project INSU – Alps)
- exhumation of the Beni Bousera peridotites (Morocco; PhD of Abdelkhaleq Afiri; *publication in press in Geodinamica Acta*)

ANALYSING METAMORPHIC ROCKS

Equilibrium model of metamorphism

The underlying principle for using phase equilibrium modelling in metamorphic petrology is that all geological systems tend to achieve equilibrium. At equilibrium the energy of the system is minimized. The character, proportions and chemical compositions of the phases involved in the system do not change with time and are characteristic of the conditions at which equilibrium was attained. Attaining equilibrium implies therefore modifying phase proportions and compositions through diffusion of chemical components between the phases (minerals, fluids and liquids). As soon as the conditions (e.g. pressure, temperature) change, the system will immediately tend to a new equilibrium state. But since diffusion is involved, the *scale* at which the equilibrium will be achieved depends on the particular conditions (especially the *temperature*), on the character of the phases involved (e.g. diffusion in fluids is much faster than in solids), and on the available *time*. If the conditions change rapidly, the scale of equilibration will be small. However, it can be argued that even in this case the system will develop *local equilibria* – small domains where equilibrium is achieved or approached (e.g. Korzhinskii 1959; Thompson 1959). The equilibrium phase (mineral) assemblages and compositions can then be identified through a rigorous petrological analysis and the principles of equilibrium thermodynamics may be applied in order to understand the rock and determine the conditions of formation (cf. Powell 1978).

Petrography

In order to determine correctly the conditions of formation, the identification of the equilibrium mineral assemblages and the scale of equilibration is therefore necessary. However, this is not a straightforward exercise in complex geological systems and implies a certain amount of more or less subjective interpretation. Due to the relatively low temperatures and the relative rapidity at which many geological processes occur (in particular in the crust), complete equilibration is the exception rather than the rule in most crustal rocks. Instead, the rocks tend to partially preserve a sequence of local equilibria, achieved successively during their evolution. This is obviously a chance, since it offers a geologist a glance into the past of the rock. Nevertheless, understanding correctly the message requires careful and commonly time-consuming observations, and an open mind ready to reconsider previous interpretations in the light of new evidence. Such an evidence/suggestion may come from other domains of the same thin-section, from associated samples, or, importantly, be inferred from the results of numerical modelling of phase equilibria.

Inclusions

Among the textures most commonly used to infer the history of metamorphic rocks are mineral inclusions in porphyroblasts. Their interpretation may seem straightforward – inclusions should be older than matrix minerals, inclusions in the porphyroblast core should be older than those situated close to the rim. Indeed, inclusion sequences have been successfully used to infer coherent, reasonable P–T evolutions (e.g. Thompson et al. 1977; Štípská et al. 2006). However, in many instances inclusions may be misinterpreted (e.g. Vernon et al. 2008). Are inclusions older than or contemporaneous with the porphyroblasts? Could they be younger? Are polymineralic inclusion clusters the image of the pre-existing

assemblage or the result of reequilibration / destabilisation of another mineral? Some of these aspects are discussed in the following figures (Figs. 1-4).

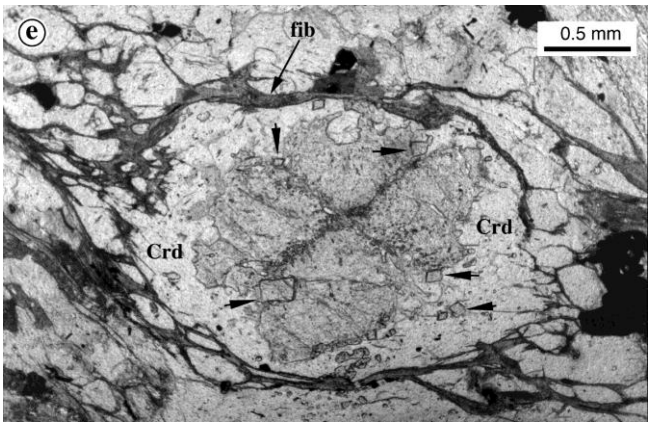


Fig. 1: Subhedral crystal of chiastolitic andalusite, surrounded by cordierite and wrapped by a fibrolitic sillimanite (fib)-bearing foliation (Marble Hall, Transvaal, Pitra and de Waal 2001). It contains relatively coarse inclusions of prismatic sillimanite, pointed by black arrows (besides the tiny inclusions of quartz and graphite defining the chiastolite cross). A straightforward interpretation of the crystallisation sequence would be: prismatic sillimanite → andalusite → cordierite → fibrolitic sillimanite. This would imply a complex P–T path involving two high T stages separated by a period of cooling, during which chiastolite would crystallise.

However, chiastolite is only reported from rocks having undergone prograde metamorphism, whereas late, retrograde andalusite never displays the chiastolite texture. This may be attributed to the increase of grain size during metamorphism. Only very small minerals may be incorporated in the chiastolite texture – such small crystals are generally found in rocks that have not been previously metamorphosed. This argues against the prismatic sillimanite being older than the chiastolite. But then how can it be found *inside* the chiastolite crystals?!

A careful observation reveals that all sillimanite prisms have the same crystallographic orientation, in this case with [001] sub-normal to the photograph, as suggested by the lozenge shape characteristic for (001) sections. Interestingly, the chiastolite prism has the same orientation. Consequently, the texture may be attributed to a topotactic replacement of chiastolite by prismatic andalusite – known (Vernon 1987), but clearly not trivial… In this case, the first-order P–T path may be interpreted in terms of a much simpler, single prograde history. Chiastolitic andalusite crystallised during a progressive prograde metamorphism of an unmetamorphosed sediment. Subsequently, during further temperature increase, andalusite interior was partly converted to prismatic sillimanite. Such textures are attributed to high temperatures and dry environments (e.g. Carlson and Rosenfeld 1981). Meanwhile, fibrolite grew locally along planes where fluids were present.

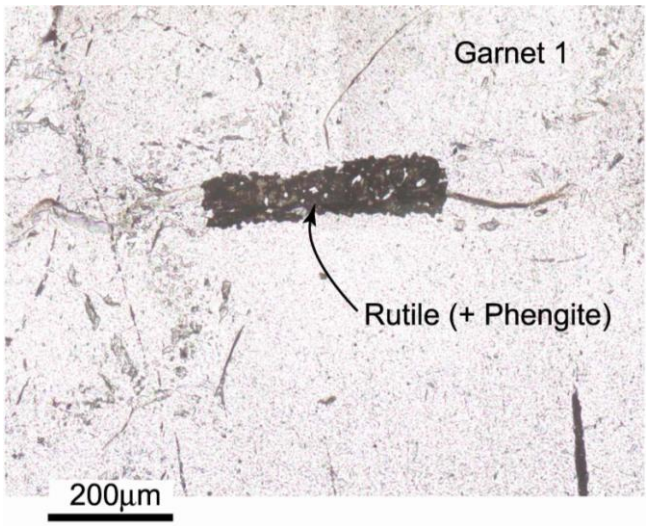


Fig. 2: Rutile + phengite inclusion cluster in a garnet from Gran Paradiso (Italian Alps). Owing to the particular form of the cluster and considering subsequent phase equilibrium modelling, these inclusions are inferred to have formed *after* the growth of this garnet, replacing the original inclusion of ilmenite at a moment when it was connected by fractures (now sealed by a second garnet generation) to the matrix (Le Bayon et al. 2006). The implications for the P–T history are not negligible. Whereas rutile (*a fortiori* with phengite) points commonly to rather HP-LT conditions, ilmenite is reputed stable at LP-HT conditions.

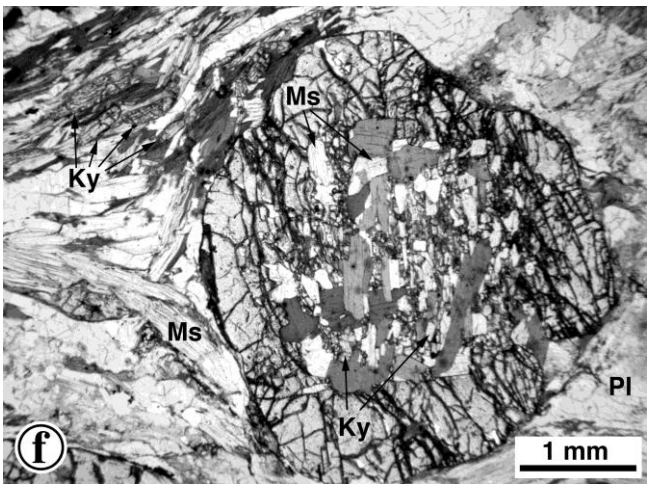


Fig. 3: “Spongy” garnet from the Upper Allochthon unit of the Champtoceaux complex (Armorican massif) (Pitra et al. 2010a). The poikilitic core contains “inclusions” of kyanite and large crystals of biotite and white mica. These inclusions are the same, in mineralogy, chemical composition and size, as the matrix minerals. They generally lack preferred orientation and take the appearance of a mineral assemblage statically replacing the garnet cores. These “inclusions” are therefore also inferred to have developed *after* the garnet crystal. This interpretation is supported by the following observations in neighbouring domains of the thin-section.

In some rare garnet crystals, the cores are preserved. They contain an inclusion assemblage that has a different grain size and mineral character (among others small crystals of epidote and staurolite). The chemical composition of the core also differs strongly from that of the garnet rim. This suggests that the core formed at different conditions than the garnet rim. It was “farther” from equilibrium at the conditions when the matrix formed, and hence more liable to destabilisation than the rim, which survived.

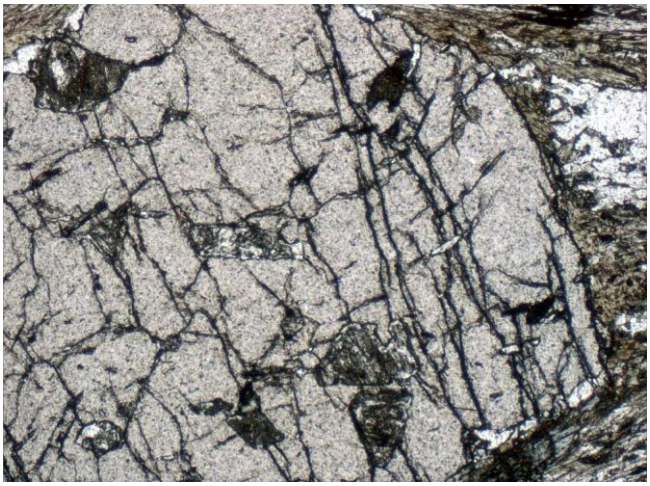


Fig. 4: Epidote+paragonite-dominated inclusion clusters in garnet (Syros, Cyclades, MSc of Lorraine Tual). Locally, their lozenge shape suggests they are pseudomorphs after lawsonite (cf. Ballèvre et al. 2003). In other instances, this identification is much less straightforward. Yet, it is of paramount importance for the interpretation of the P–T evolution of the rocks. The long dimension of the photograph is 2.85 mm.

Coronae

Coronae are mono- or commonly polymineralic layers developing at the interface between minerals, typically between a porphyroblast and the surrounding matrix. In general, they comprise finer-grained crystals that partially replace the coarse-grained minerals (Figs. 5, 6). The interpretation of such textures is relatively straightforward: they are thought to reflect changes in the mineral composition of the rock, as a result of disequilibrium between the original minerals, related to changing P–T conditions, typically decompression accompanied by cooling. They are therefore textures that denote reaction. The spatial distribution of the minerals suggests what are the reactants and the products. The mineral assemblage present in the corona reflects the new equilibrium assemblage, to which the rock tends. However, as suggested by the fine grain-size and the localised character of the texture, this equilibrium is local and different types of coronae may be observed in a single thin section. Since the replacement is commonly only partial, both products and reactants can be observed, allowing to infer not only one point in the P–T diagram, but a segment of the P–T path or at least an evolutionary trend followed by the rock.

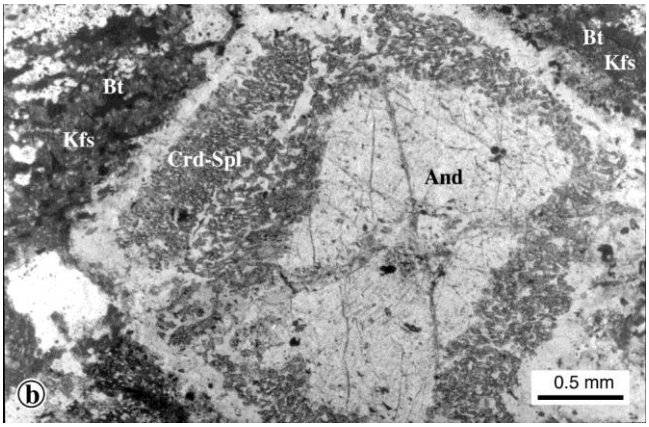


Fig. 5: A corona texture consisting of an outer layer of cordierite and an inner layer of cordierite+spinel symplectite, which developed at the expense of a chiastolitic andalusite. It reflects a reaction between the latter and the silica-undersaturated, biotite rich matrix. Marble Hall, Transvaal (Pitra and de Waal 2001). Detailed textural analysis (cf. Fig. 1) and calculated phase diagrams considerations allowed to suggest that rather than the commonly expected decompression and/or cooling, this texture is related to a *prograde* evolution (isobaric heating), although subsequent decompression may have been responsible for the preservation of the texture (Johnson et al. 2004).

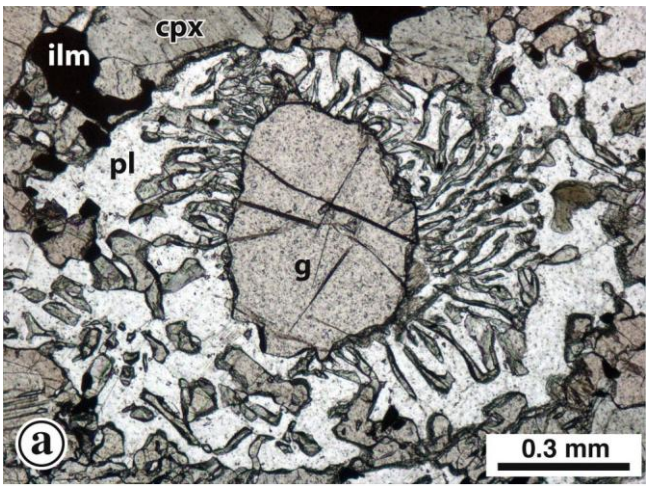


Fig. 6: A plagioclase + orthopyroxene symplectite between garnet and clinopyroxene in a metabasic granulite from the Man Shield, Ivory Coast. The symplectites also includes a secondary clinopyroxene, green secondary amphibole, magnetite and ilmenite. This relatively classic texture is related to the decompression and cooling of a high pressure granulite (Pitra et al. 2010b).

In conclusion, it is important to emphasize that the quality of the petrographical work determines *critically* the quality and validity of the interpretations based on the results of the phase equilibria modelling.

Mineral composition

Crystals of one mineral species may form successively at different moments of the metamorphic evolution of the rock. These different mineral generations commonly display different chemical compositions, depending on the P–T conditions and/or on the scale of equilibration, which both do or can change in time. A careful examination of the chemical compositions of all minerals and an attempt to associate the observed variations with different textural positions of the crystal are crucial for understanding the evolution of the rock. Although an electron microprobe analysis in point mode is in general sufficient, X-ray maps are an indispensable tool for revealing heterogeneities in optically homogeneous crystals (Figs. 7; 8) or chemical zoning (see below).

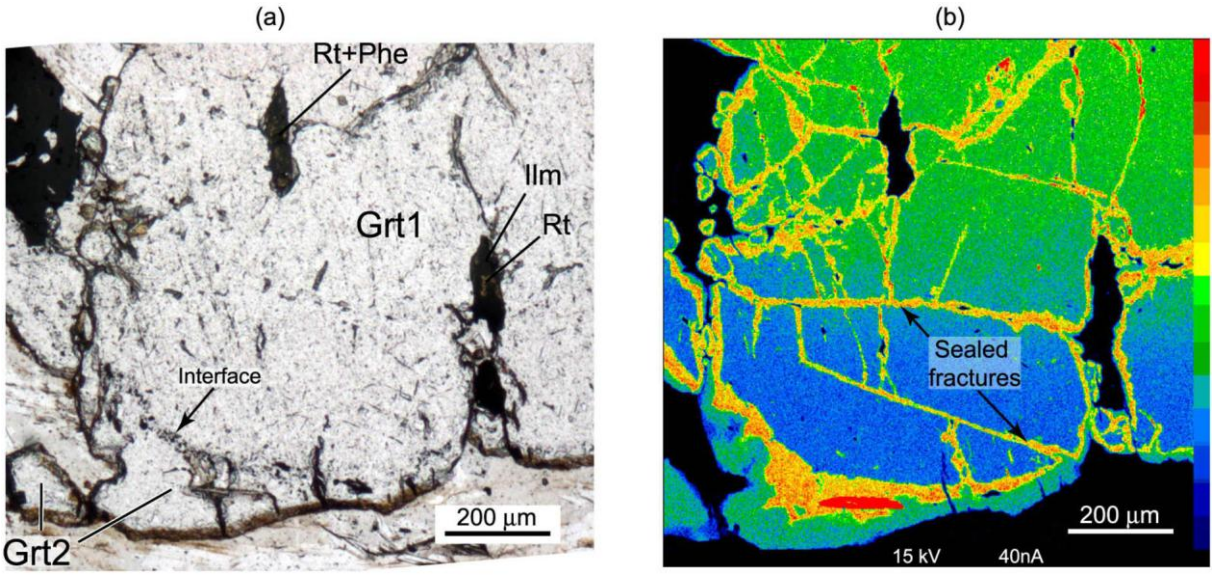


Fig. 7: Microphotograph (a) and an X-ray map of Ca concentration (b) of a large garnet porphyroblast from Gran Paradiso (Italian Alps, Le Bayon et al. 2006). The X-ray map reveals that the garnet rims (Grt2; visible also in an optical microscope) display strikingly different compositions, attributable to a crystallisation at completely different P–T conditions. What is not seen in an optical microscope, are the numerous fractures cutting through the garnet core (Grt1) and sealed by garnet with the composition of the crystal rims (Grt2). This allows to explain the replacement of the original ilmenite inclusions by the rutile+phengite clusters (Fig. 2) and reveals an unsuspected aspect of the rock's history.

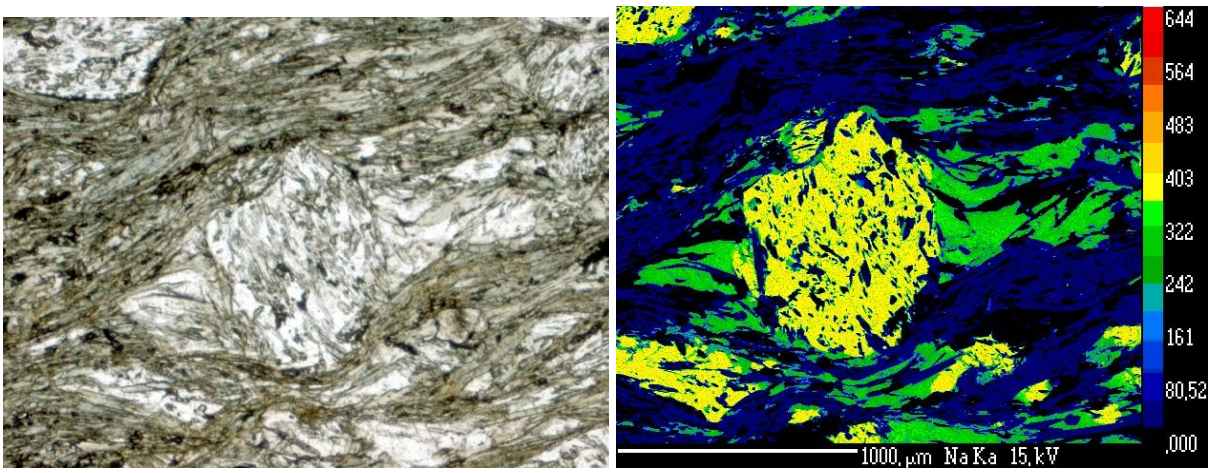


Fig. 8: Microphotograph (left) and an X-ray map of Na concentration of a metabasic rock from the Rhodope Mountains. The development of oligoclase crystallisation tails (green) around albite crystals (yellow) suggests a syndeformational increase of temperature (roughly speaking from the greenschist- to the amphibolite-facies). Work in progress…

Chemical zoning

The best-known example of the mineral composition evolution along a P–T path is the development of chemical zoning. Two end-member types of zoning are distinguished (e.g. Tracy 1982). *Growth zoning* corresponds to the case, where the equilibrium composition of a mineral changes progressively as the metamorphic conditions evolve, and each successive layer of the growing crystal has a different chemical composition. In order to be preserved, growth zoning requires minerals characterised by a slow intracrystalline diffusion, typically garnets. *Diffusional zoning* represents the case where the composition of a mineral (previously homogeneous or not) is progressively changed by intracrystalline diffusion. This is generally driven by reaction of the surface of the crystal with matrix minerals. A typical example is the increase of the Mn content at the rim of a progressively resorbed garnet, due to the strong partitioning of Mn into garnet. However, in the case of a previously zoned crystal, chemical potential gradients between the successive crystal 'layers' may be the driving force. Intracrystalline diffusion then modifies the existing chemical differences (i.e. the zoning) and tends to homogenize the crystal chemistry.

When preserved, growth zoning may be used, in combination with calculated phase diagrams, to understand and quantify the prograde evolution of metamorphic rocks (e.g. Vance and Mahar 1998; Štípská and Powell 2005; Le Bayon et al. 2006; Štípská et al. 2006). Despite the apparent success of this method, more caution is possibly needed in using zoned crystals. Recent work tends to suggest that the diffusional alteration of an existing zoning even in minerals like garnet may be relatively rapid and more important than previously thought (Caddick et al. 2010). Since the resetting is commonly only partial, the resulting compositions reflect then neither the original nor the final metamorphic conditions. Nevertheless, since the patterns of growth and diffusion zoning may be in general distinguished, crystal-scale zoning trends may still be used to infer the general tendency and at least qualitatively constrain the P–T evolution (Fig. 9). Correct identification of these features is essential for accurately interpreting the metamorphic record.

"Simple" minerals

Attention should also be paid to the composition of reputedly "pure" minerals. A good example is sphene (titanite). Although it is nearly pure $CaTiSiO_5$, substitutions of Fe and Al for Ti are relatively common, in particular at high pressures (e.g. Franz and Spear 1985; Holényi and Annerstein 1987; Enami et al. 1993; Tropper et al. 2002; Harlov et al. 2006). Although they commonly do not excess a couple of weight %, their influence on the stability of sphene may be significant. Taking these departures from ideality into account may allow to understand some apparent incompatibilities between the observations and the predictions of the calculated phase diagrams.

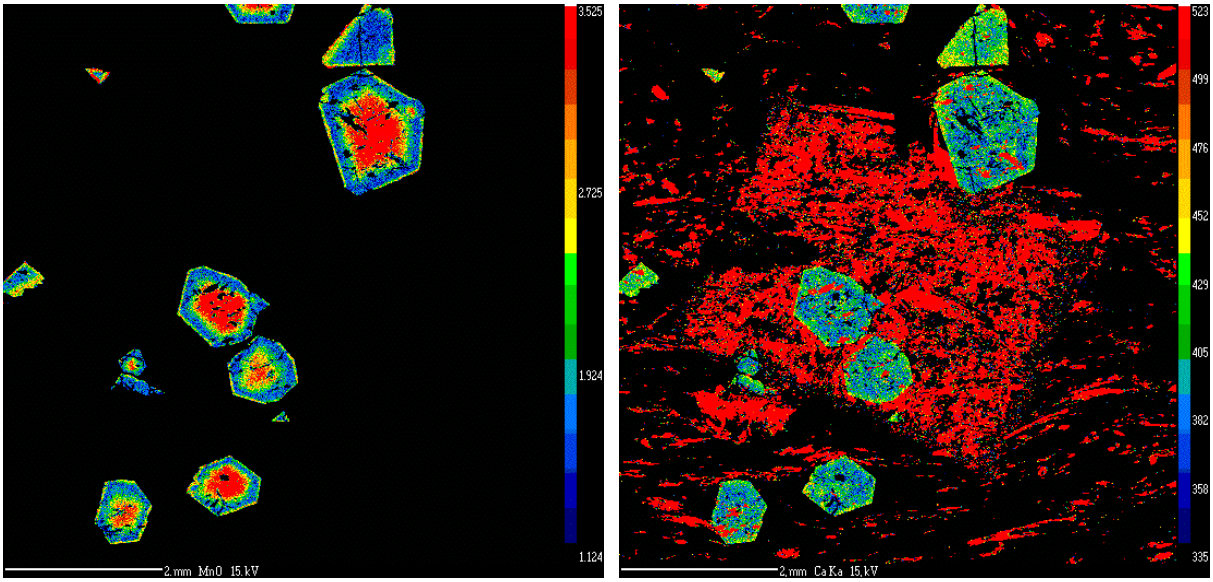


Fig. 9: X-ray maps showing Mn and Ca zoning in garnets in a lawsonite-blueschist from Syros (Greece; collaboration with Melody Philippon). Garnets included in the pseudomorphed lawsonite crystal (red-dominated rectangle in the Ca-map, right) display the same type of zoning as those in the matrix, including the thin high-Mn and high-Ca rim, interpreted as the result of partial resorption. This may suggest that lawsonite only started to crystallise when garnet was partly resorbed after its growth. Generally speaking, this would suggest lawsonite growth during decompression and/or cooling.

However, lawsonite crystals are entirely pseudomorphed. The replacement of lawsonite by an epidote + paragonite + chlorite ± albite mixture would allow the communication of the garnet inclusions with the matrix and the development of diffusion zoning in the rim. It is therefore possible that garnet resorption is contemporaneous with the destabilisation of lawsonite. Lawsonite would then have grown at the metamorphic peak, at the end of garnet crystallisation, but before its resorption. A close study of the calculated phase diagrams can help discriminate between the two hypotheses.

Minding the structures

If the goal of a metamorphic study is to contribute to the understanding of the tectonic evolution of a region (rather than methodological development, explaining the formation of particular textures, etc.), the results must be linked with a structural framework. This requires attentive structurally-oriented field work, collecting oriented samples, cutting the thin sections in appropriate orientations and last, but not least, diligent petrographical work aiming to comprehend the relations between different mineral assemblages and particular structures.

The petrographic (or microscopic) part of this exercise involves deciphering the relations between foliations and metamorphic minerals, in particular porphyroblasts (the "crystallisation–deformation relations"), interpreting foliation superpositions and shear-sense criteria in thin sections – and telling them apart. Despite the classic nature of this exercise, its importance is commonly underestimated, which may lead to erroneous interpretations (Fig. 10).

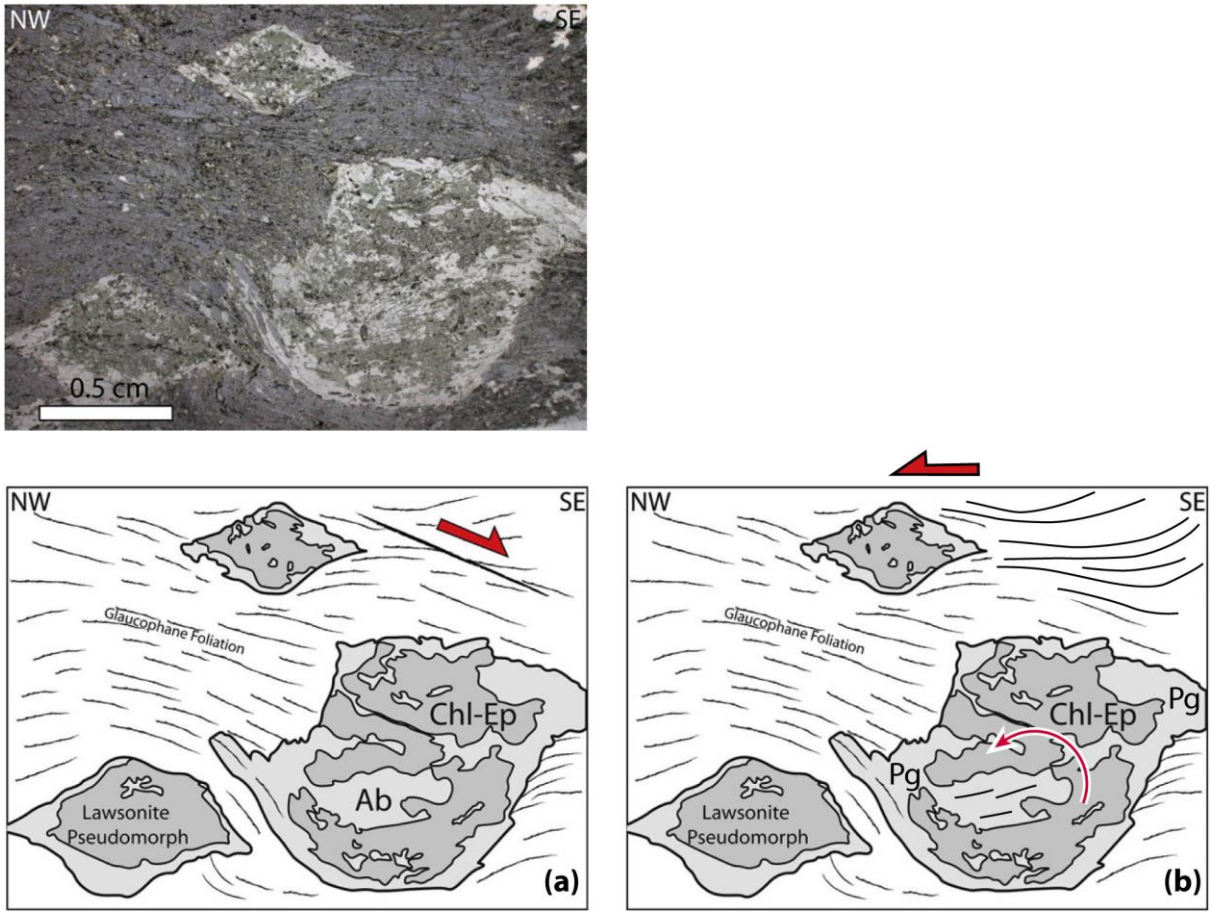


Fig. 10: An example of how underestimating the petrographic analysis may result in unreliable descriptions and interpretations. The intention is not to provide an exhaustive list of papers containing such misinterpretations, nor to imply that the cited paper is less than excellent in other respects. Rather, I merely wish to emphasize the importance and difficulties of an accurate textural analysis in metamorphic rocks.

Microphotograph of several pseudomorphed lawsonite crystals in a glaucophane–epidote blueschist from Ile de Groix (Armorican Massif). (a) An interpretation proposed by Philippon et al. (2009). (b) An alternative interpretation. Several differences merit to be emphasized:

Although albite is locally present in the core of the pseudomorphs, paragonite is the dominant mineral, in particular in the outer part of the pseudomorphs (cf. Ballèvre et al. 2003). Although this has no direct implication for the conclusions presented by the authors, albite is in general stable at significantly lower pressures than paragonite. Albite-dominated pseudomorphs after lawsonite might have therefore developed at much lower pressures than those with paragonite.

No grain-size reduction and related decrease of the interfolial spacing, characteristic for shear zones, is observed in the "shear band" in the upper right corner of the figure. Several glaucophane prisms pass quietly across the supposed shear band. The feature should be interpreted as a simple undulation of the foliation with no kinematic significance. Interestingly, similar foliation inflections that *appear* as, but are not shear zones are described from experiments involving porphyroblast rotation (Van Den Driessche and Brun, 1987; cf. below).

A detailed observation of the thin section reveals that small preferentially oriented glaucophane crystals are present inside the large pseudomorph and define an internal foliation oblique to but continuous with the matrix foliation. They are interpreted as inclusions in the original lawsonite crystal (cf. Ballèvre et al. 2003). The orientation of this internal foliation suggests that the lawsonite crystal partly rotated during the shear deformation (if one admits that porphyroblasts do rotate during shear deformation…). If so, the sense of rotation and hence the sense of shear is left-lateral, i.e. top-to-the-NW, opposite to that inferred in (a).

Although not explicitly noted, the tails at the top right and bottom left end of the large lawsonite pseudomorph are probably interpreted as "sigma-type" "pressure shadows" in (a), supporting the top-to-the-SE sense of shear. Yet, it can be argued that the geometry of the two tails appears different and the right one is not entirely visible, making the interpretation hazardous. Furthermore, the geometry of the left tail resembles more the "delta-type" or "rolling structures" (Van Den Driessche 1986; Van Den Driessche and Brun 1987), in agreement with the rotation inferred from the internal foliation, suggesting again an opposite, top-to-the-NW sense of shear.

As another example, Lexa et al. (2004) have demonstrated that many sections across samples with folded foliations exhibit shear band-like geometry, although they are not real shear zones. They have shown how using these apparent shear bands as shear sense indicators lead to misunderstanding an important part of the tectonic evolution of the western Carpathians.

On the other hand, accurate interpretation of the crystallisation–deformation relations may reveal the relative timing of foliation formation (and hence a particular deformation event) with respect to porphyroblast growth. If the porphyroblasts form at a particular locus of the P–T path (e.g. the pressure or temperature peak), then the deformation may be attributed to a specific part of the orogenic process (subduction, collision, exhumation, etc.) (Fig. 11, 12).

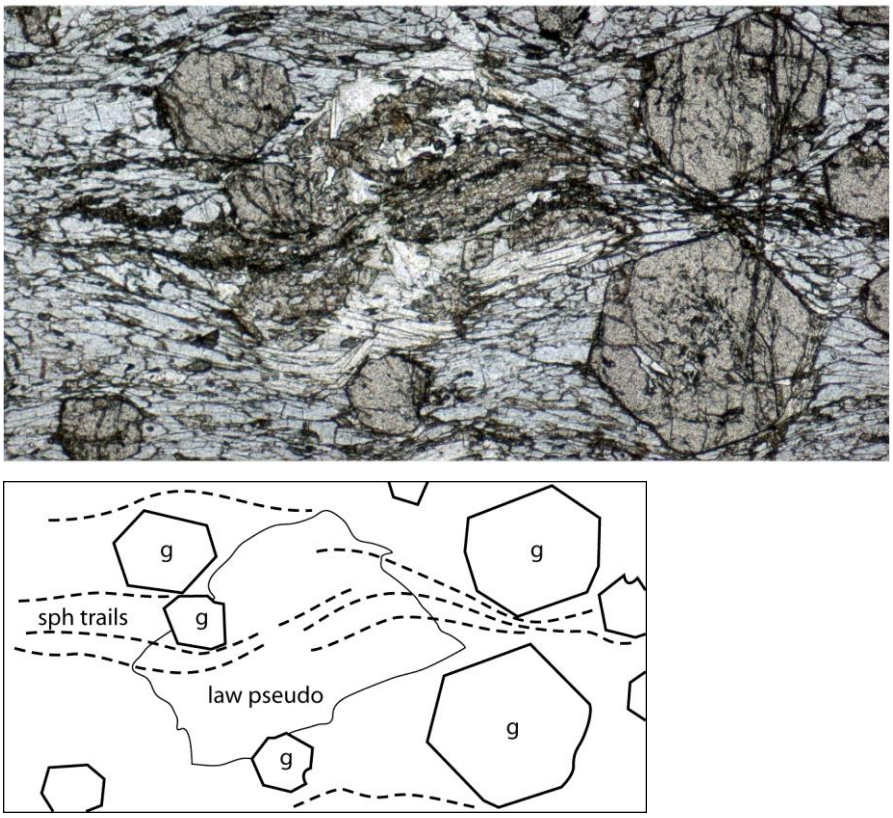


Fig. 11: Microphotograph and an interpretative drawing of a fine-grained blueschist from Ile de Groix (described in Ballèvre et al., 2003). The matrix foliation is defined by glaucophane, epidote and titanite ('sph trails'). It wraps gently around lozenge-shaped white aggregates (cf. Fig. 10) that are irregularly dispersed in the rock, do not show a preferential shape orientation, and are interpreted as pseudomorphs after lawsonite ('law pseudo'). This indicates that some ductile deformation took place during or after the growth of lawsonite. The pseudomorphs consist of an aggregate of paragonite, chlorite and epidote. They also contain glaucophane, garnet (g) and titanite (sph). Glaucophane crystals, titanite and some of the epidote grains are aligned parallel to each other, and define an internal schistosity ('sph trails'), interpreted as a relic foliation that has been overgrown by the pseudomorphed porphyroblasts (cf. Fig. 10). This internal foliation is slightly curved and continuous with the matrix foliation, suggesting that lawsonite grew syn-kinematically in a foliated matrix containing glaucophane, epidote and garnet.

Euhedral garnet crystals contain inclusions of epidote, actinolite, glaucophane, abundant titanite and minor rutile with some quartz and apatite. Core inclusions are not aligned, but rim inclusions tend to be parallel to the matrix foliation, suggesting foliation development at a late stage of garnet growth. Further indication in favour of a late foliation development during garnet growth is provided by the titanite aggregates, which display irregular shapes in garnet cores, then become flattened towards the garnet rims, and are continuous with the alignment of titanite grains defining the matrix foliation. In short, garnet growth began before and continued during ductile deformation, while the growth of lawsonite took place during ductile deformation.

The pseudomorphic replacement of lawsonite is interpreted as post-kinematic as suggested by the lack of preferred orientation of the breakdown products in the pseudomorphs and the preserved shape of the original crystals (cf. Fig. 10). Similarly, local partial replacement of garnet by unoriented chlorite–albite aggregates post-dates the development of the foliation.

To sum up, the paragenetic history of the sample is characterized by three stages, namely (i) pre-kinematic garnet cores in equilibrium with actinolite, glaucophane, epidote, and titanite, (ii) syn-kinematic lawsonite and garnet rims in equilibrium with glaucophane, epidote, and (iii) breakdown of lawsonite into chlorite–epidote–paragonite, and chlorite–albite growth at the expense of garnet. Ductile deformation began during garnet growth and ceased before stage (iii).

Subsequent numerical modelling of phase equilibria (Ballèvre et al. 2003) suggests that the growth of garnet and lawsonite occurred along the prograde part of the P–T path, and culminated at the pressure peak. This allows to attribute the development of the foliation (and the possibly associated shear-sense criteria) in this sample to the stage when the rock was going down into the subduction zone. As suggested by Philippon et al. (2009), the exhumation of the Ile de Groix metamorphic complex occurred under greenschist facies conditions with an opposed kinematics, localised and documented in other parts of the island.

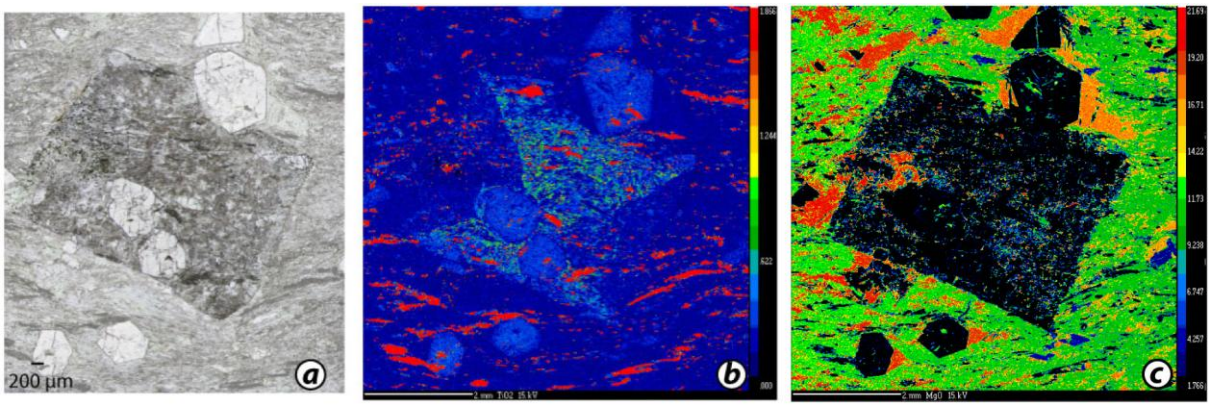


Fig. 12: Lawsonite-bearing blueschist from Syros (Greece; collaboration with Melody Philippon). Microphotograph (a) and X-ray maps for Ti (b) and Mg (c). Similar features as in Fig. 11 can be observed.

The foliation is defined by the preferred orientation of glaucophane, epidote, muscovite, chlorite, and stretched clusters of titanite (red in (b)). This foliation wraps gently around mostly euhedral crystals of garnet and lozenge-shaped aggregates containing epidote, chlorite, paragonite and locally albite, interpreted as pseudomorphs after lawsonite. The pseudomorphs also contain crystals of glaucophane, epidote and stretched clusters of titanite that define a curved internal foliation, generally oblique to but continuous with the matrix foliation. Locally, garnet crystals are also included in the pseudomorphs. The pseudomorphs display a hourglass-shaped distribution of Ti (b), reminiscent of the sector zoning observed in fresh lawsonite crystals (Ueno 1999).

Garnet is nearly euhedral and contains inclusions of glaucophane, epidote, muscovite and titanite that are mostly unoriented, or display rarely a weak preferred orientation, continuous with the matrix foliation. Crystallisation tails of chlorite (orange/red in (c)), parallel to the foliation are present around matrix garnets, but are absent around garnets included in the lawsonite pseudomorphs.

The microtextural features suggest that garnet crystallised before the main deformation. The subsequent crystallisation of lawsonite was contemporaneous with the development of the foliation, which formed mostly after the crystallisation of garnet. Accordingly, crystallisation tails of chlorite developed around garnet in the matrix, but not around the crystals included in and shielded by the lawsonite crystals. Lawsonite breakdown occurred after the deformation, as evidenced by the preservation of the euhedral shape of the pseudomorphs and the sector zoning. The chemical zoning of garnet suggests a growth along a prograde P–T path (Fig. 9). The deformation occurred in the lawsonite stability field, on the prograde portion of the P–T path, as indicated by the zoning of garnet (Fig. 9) and the preservation of lawsonite pseudomorphs. It is therefore related to subduction.

It is only through integrating the metamorphic record with structural data (as well as, obviously, the geochronological, magmatic, sedimentary, geophysical, etc. information) that a reliable tectonic picture of a region may be drawn. From this point of view, it is regrettable that large-scale thermomechanical numerical modelling, or exploring the crust–mantle or lithosphere–atmosphere interactions, for example, rather than field-based structural geology are viewed as the exclusive future of tectonics and the young generation of tectonicians is more and more encouraged in this direction. It is then increasingly common – but sometimes possibly unfortunate – that the responsibility of a sound structural analysis and the subsequent tectonic interpretation relies solely on the metamorphic petrologist.

CONSTRAINING THE CONDITIONS OF METAMORPHISM

In the framework of understanding the geodynamic evolution of a region, one of the primary goals of metamorphic petrology is to give quantitative or qualitative constraints on the pressure – temperature (P–T) conditions of formation of metamorphic rocks and, if possible, their evolution in time. Indeed, despite the locally important problems of strain-induced tectonic overpressure (e.g. Petrini and Podladchikov 2000; Mancktelow 2008; Raimbourg and Kimura 2008; Li et al. 2010), pressure can be – at the first order – directly correlated with depth (z) through the lithostatic pressure model ($P = \rho g z$, where ρ is the density of the overlying rock column). Knowing the temperature at a given depth allows calculating the geothermal gradient, which can, in turn, be correlated with a particular geodynamic setting (e.g. Miyashiro 1961, 1973; Winter 2001). This task can be approached from two directions: using geothermobarometry, or using phase diagrams.

Geothermobarometry

The principle of 'classic' geothermobarometry is using two, in general directly (experimentally) calibrated equilibria written between end-members of phases inferred in equilibrium in the given rock (or equilibration volume) and reading the equilibration P–T conditions from their intersection (e.g. garnet–biotite Fe-Mg exchange combined with the garnet–aluminium silicate–quartz–plagioclase net-transfer equilibrium). The reason for the success of this method – in particular among non-petrologists – resides in its straightforwardness: analyse a couple of grains on a microprobe – calculate a couple of simple compositional parameters – use an excel sheet – get a result. However, this straightforwardness represents also the major danger of this method: whatever the input parameters, one *always* gets a result that can be directly used, unless the resulting numbers are completely unrealistic (e.g. negative). No cross-check, beyond possibly the common petrological sense, is available.

With the appearance of internally-consistent sets of thermodynamic data (Powell and Holland 1985; Berman 1988) and associated computer programmes, the application of multi-equilibrium geothermobarometry became possible (Powell and Holland 1988; Berman 1991). The use of thermodynamic datasets allows to take into account many more equilibria than those directly experimentally calibrated and obtain then a better constrained result. Moreover, multi-equilibrium geothermobarometry also gives the possibility to estimate the coherence of the data and hence whether or not the used minerals approached equilibrium. Two different approaches are dominant in the present-day petrological literature – the method used by Berman and the programme TWEEQU on the one hand, and Powell and Holland and the programme THERMOCALC on the other hand. The major difference concerns the statistical treatment of the results and the uncertainties. TWEEQU calculates *all* the equilibria between the end-members of the phases inferred to be in equilibrium and plots them as lines in a P–T diagram. This 'tightness' of the intersection of the lines allows a visual *qualitative* estimation of the coherence of the input data and the uncertainty. However, many of the equilibria are necessarily linear combinations of others, and the final graphical output gives a false impression of robustness. On the other hand, the "average P–T" method of THERMOCALC uses only an *independent set* of equilibria (from which all the other possible equilibria can be calculated) and a robust statistical treatment to indicate *quantitatively* the uncertainty on the result, and the 'goodness of the fit' of the data (to what extent the data are probable to reflect

an equilibrium / suitable to be used together) (Powell and Holland 1994; Powell and Holland 2008).

Nevertheless, despite the superiority of the multi-equilibrium methods over 'classic' geothermobarometry, the result is always one point in the P–T diagram and it is in general not possible to obtain quantitative information about the *P–T evolution* of the rock. Furthermore, additional problems comprise (e.g. Spear 1993; Winter 2001)

- the *equilibrium chemical composition* of the phases: (i) problem of identification of the part of a chemically zoned crystals that was in equilibrium with the other minerals; (ii) problem of the diffusional modification of the equilibrium composition (reequilibration), and the related problem of blocking temperatures (temperatures below which the diffusion is too slow to modify the chemical composition of the phases)
- *extrapolating* the experimentally calibrated equilibrium (i) to minerals of different composition (the effect of additional components – e.g. Ca, Mn in garnet); (ii) to P–T conditions different from the experimental ones.

Yet, geothermobarometry can yield interesting information in the hands of a careful user and the relative simplicity and rapidity of use can surely be an advantage, in particular in the early stages of a project. However, as noted above, despite the apparent simplicity of the method, a proper textural analysis and interpretation, understanding the compositional heterogeneity and the reaction history of the rock are essential prerequisites for geothermobarometry to yield any useful results.

Phase diagrams

The mineral composition of metamorphic rocks reflects just as much the physical equilibration conditions (P–T), as the chemical system – i.e. the chemical composition of the rock (or the equilibration volume), possibly modified by externally-derived fluids or liquids. These two fundamental aspects are approached by the two classic end-member types of phase diagrams used in petrology:

- the *pressure – temperature diagram* (or P–T projection), typically representing the position of various chemical reactions, which subdivide the P–T space into domains characterised by the possible stability of particular mineral associations. Although such diagrams may be useful to understand first order principles, they only represent the univariant, discontinuous reactions, whereas most mineral changes in complex systems are achieved via continuous (higher variance) reactions. Furthermore, in complex systems, such diagrams are difficult to read because of the large number of reactions present and the large number of phases involved on each of them (Fig. 13).
- the isobaric, isothermal *compatibility diagram*, representing all the mineral assemblages in a given chemical system that are *compatible* (in rocks of different bulk composition!) at the given pressure and temperature.

In order to understand completely a rock, both aspects need to be considered. A simple example of such a combination are the binary temperature (or pressure) – composition diagrams used in magmatic petrology to explain the crystallisation / melting relations in the solidus – liquidus region. The concept of combining these aspects in one diagram is brought to the uttermost level in the diagrams known as "pseudosections".

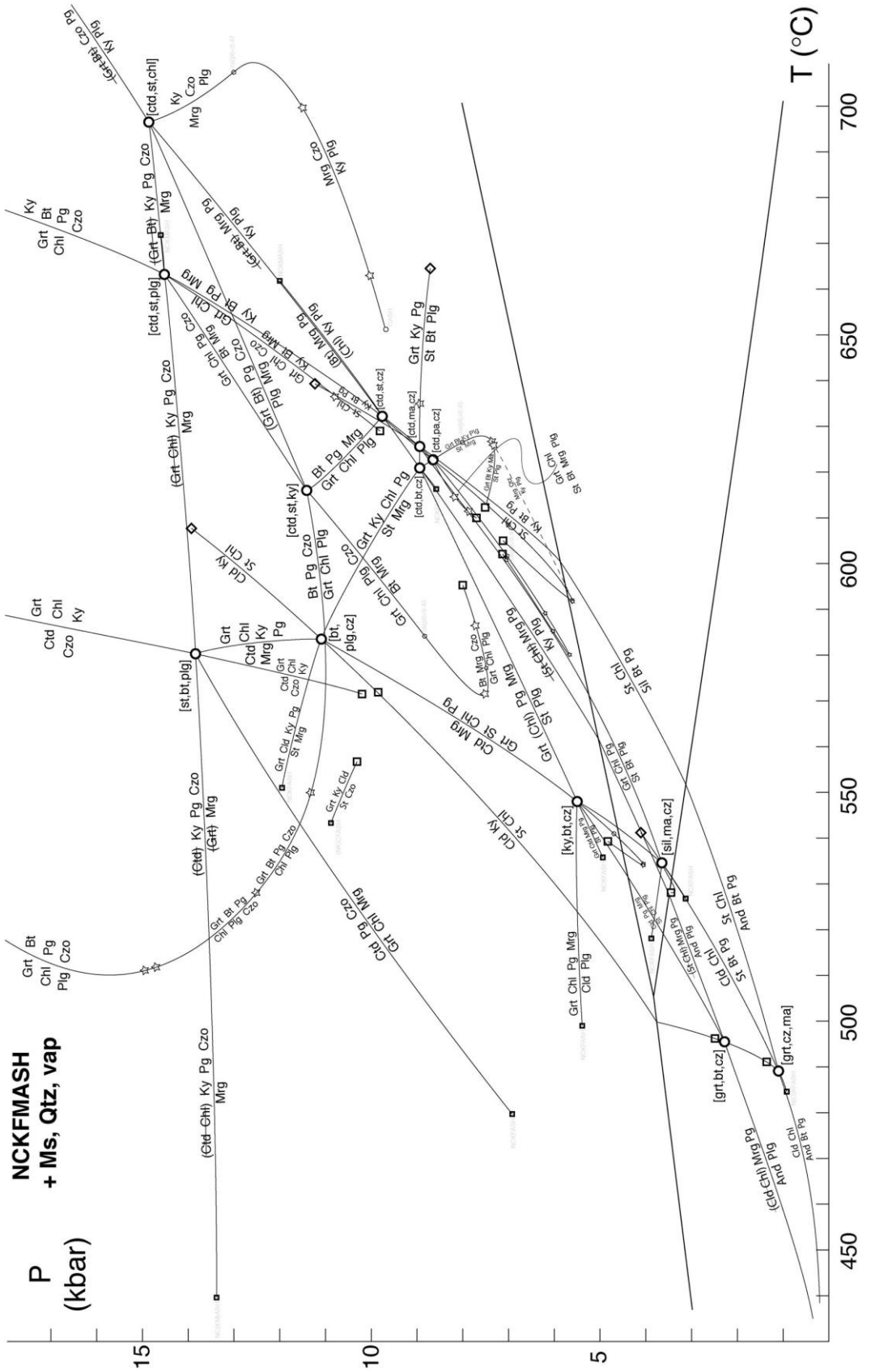


Fig. 13: Example of a P–T projection ("petrogenetic grid") calculated with THERMOCALC in the model system NCKFMASH. H_2O, quartz and muscovite are considered in excess. White stars represent singular points, where one of the phases shifts on the other side of the reaction (Worley and Powell 1998). Although this diagram may be a useful base for calculating pseudosections, it is in itself difficult to use for interpreting metamorphic rocks.

PSEUDOSECTIONS

Pseudosections are equilibrium phase diagrams that directly represent the domains of stability of specific phase assemblages in a rock (or its part) of a specified bulk chemical composition (or a range of compositions along a particular compositional vector). After the pioneering work of Hensen (1971), and the exploration of this territory by some isolated workers (e.g. Hudson 1980; Hudson and Harte 1985) it was the development of the internally-consistent thermodynamic dataset and the associated software THERMOCALC at the end of the 1980s (Powell and Holland 1985, 1988; Guiraud et al. 1990; Powell and Holland 1990) that allowed the widespread use of these diagrams for metamorphic rocks (Fig. 14).

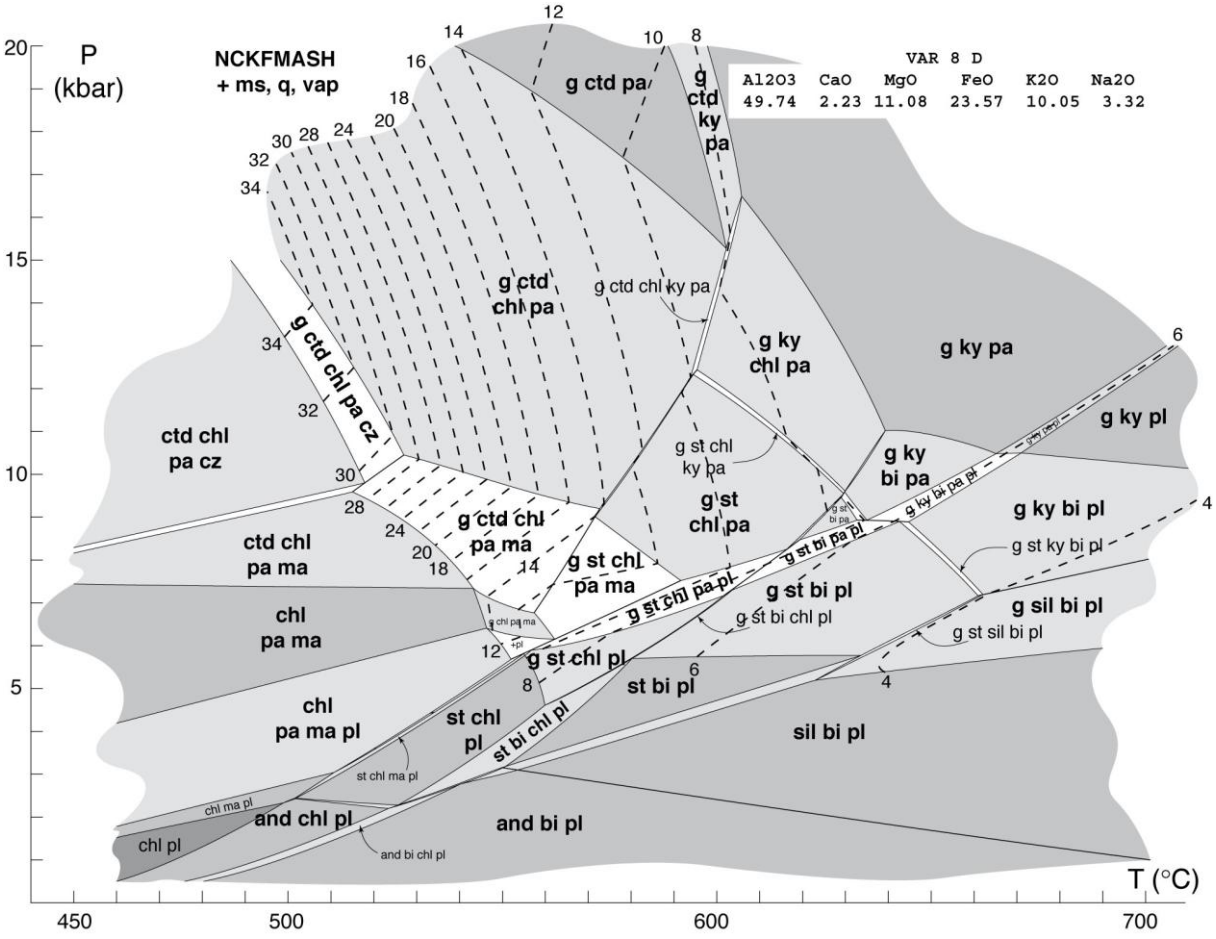


Fig. 14: Example of a P–T pseudosection calculated with THERMOCALC for a metapelitic rock from the Champtoceaux complex (cf. Pitra et al. 2010a) in the model system NCKFMASH, based on the P–T projection represented in Fig. 13. Short segments of the univariant equilibria may still be found between white (divriant) fields. The composition of the rock is represented in the upper right corner, silica is in excess. Note the considerable simplification of the diagram compared to the P–T projection. Thick dashed lines are isopleths of the grossular content in garnet.

When calculated using a thermodynamic dataset, pseudosections represent the result of a *forward* numerical modelling and are independent on the petrographic observations that can be done in the specific rock. As such, they can be used to retrieve general information about the behaviour of metamorphic rocks – e.g. the conditions and sequence of appearance and disappearance of some characteristic phases (minerals, fluids or liquids), the evolution of their chemical composition and abundance, the volume or density changes, etc. (e.g. Guiraud et al. 1990; Powell and Holland 1990; Powell et al. 1998; Guiraud et al. 2001; White et al. 2001; White and Powell 2002; Powell et al. 2005; Guiraud and Powell 2006).

However, when calculated for a particular rock, pseudosections allow to understand its metamorphic evolution through comparing the observations and the results of the numerical model. Then they enter the territory of *inverse* modelling and geothermobarometry *sensu lato* (cf. Powell and Holland 2008). That said, they are in several aspects superior to the geothermobarometric methods mentioned above:

1) Since pseudosections represent the stability domains of mineral assemblages, the first order petrographic observations (i.e. the inferred equilibrium assemblages) may be used without recourse to the chemical composition of individual phases (liable to reequilibration etc.)
2) For the same reason, even partly preserved assemblages (inclusions, partly pseudomorphed minerals, …) may be useful to infer parts of the P–T path of the rock, before and after the main equilibration stage.
3) Although the exact position of the individual stability fields is subject to uncertainty (depending on the bulk composition, on the thermodynamic dataset and its uncertainties, on the activity–composition relations and finally on the software used), the *relative* position of the fields is a robust information (e.g. Hoschek 2004; de Capitani and Petrakakis 2010). Hence, for example, the development of distinct mineral assemblages in rocks of the same chemical composition may be interpreted in terms of differences of equilibration conditions, although the absolute conditions may be undistinguishable within the uncertainty. In general, my opinion is that the *qualitative* information about the relative equilibration conditions or about the evolution of a rock is the major strength of the pseudosection approach.
4) At each point of a pseudosection, the composition and proportion of all phases may be calculated. This information, commonly expressed in the form of mineral composition or mineral proportion *isopleths*, may be used to further constrain the equilibration conditions (cf. Fig. 14).
5) Isopleths may also be used to understand the chemical zoning of minerals and use it to constrain the *evolution* of the rock (e.g. Stüwe and Powell 1995; Vance and Mahar 1998; Štípská et al. 2006; Pitra et al. 2010b).
6) Finally, given the various difficulties related to the interpretation of rock textures (some of which are outlined above), pseudosections are a valuable tool to check and reconsider one's inferences. I believe that an iterative feedback, a frequent back and forth way between petrography and phase equilibria modelling, is the best way for *understanding* metamorphic rocks.

Nevertheless, despite this eulogy, the use of pseudosections is time-consuming and several problematic aspects, shortly addressed below, deserve attention.

Choosing of the "right" bulk composition

The inconvenient of incorporating the bulk rock composition into a P–T diagram in pseudosections is that they are only valid for this particular bulk chemistry. The choice of this composition is therefore a crucial step. At first glance, the answer may seem ridiculously simple: "take your rock, crush it and have it analysed!". Indeed, rock powder chemical analyses (XRF, or more commonly ICP-AES) are commonly available and relatively inexpensive. Yet, what is the volume that should be analysed? Whereas "the bigger, the better" may work for geochemical purposes, the goal of which is, in general, to get an analysis 'representative' of large rock volumes, in particular for magmatic rocks, it commonly does not for pseudosection calculations in metamorphic rocks.

Equilibration volumes

Indeed, metamorphic rocks are commonly heterogeneous and display compositional layering, of sedimentary or metamorphic origin, lenses of quartz, albite, … or granitic material resulting from fluid or liquid percolation. Furthermore, as mentioned above, metamorphic rocks do not necessarily equilibrate at large distances and may be characterised by a multitude of relatively small *equilibration volumes*. Clearly, what is needed, is the 'bulk' composition of these equilibration volumes.

It may be very difficult to identify with certainty the equilibration volume for a particular part of a rock sample. Part of the problem lies in the different diffusivities of the different elements and hence different distances at which these elements can reach equilibrium. This issue is clearly even more present in fluid-deficient environments (characteristic e.g. for the retrograde evolution).

In apparently homogeneous rocks, analysed bulk compositions (XRF, ICP-AES,…) have proved efficient in modelling the prograde metamorphic evolution and peak mineral assemblages, because equilibration volumes are probably large at high temperatures and fluid-saturated conditions. However, the size of equilibration volumes decreases rapidly as fluids are consumed and temperature decreases during the retrograde evolution. Yet, for a reasonably homogeneous rock, mineral proportions at the metamorphic peak at, for example, thin section scale are similar to those observed at the scale of a large sample. When metamorphic conditions change, the reacting effective bulk composition will then be similar to the bulk of the sample, even if equilibration volumes are small. This should be reflected by the homogeneity of the reaction textures across the sample. If this is the case, pseudosections calculated for the analysed bulk compositions may still be used for understanding the entire metamorphic evolution. Analysed bulk compositions are therefore commonly a good starting point.

In layered rocks the solution is either to extract and analyse only the particular layer of interest, or to calculate the bulk composition from the chemical composition of the phases present and their modal proportions (determined e.g. by point counting). The treatment of lenses of quartz or quartzo-feldspathic material depends on the interpretation of their origin. If the material is believed to be externally-derived, it should be removed. If it is inferred to represent a local segregation from the rock, then the treatment depends on the segment of the rock history that we are interested in, with respect to the moment of formation of the segregations.

Zoned minerals

The presence of variations in the chemical composition of minerals of the same species reflects a lack of equilibration at the scale of observation. The presence of preserved chemical zoning in minerals is such an example. Cores of a chemically zoned garnet are clearly not in equilibrium with the matrix minerals (that may be in equilibrium with the garnet rims) and retain chemical components that are then unavailable for the equilibration of the matrix (e.g. Stüwe 1997). Consequently, these parts of the zoned crystals should be removed from the analysed bulk composition (e.g. Marmo et al. 2002), although the first order effect is commonly not impressive (Fig. 15).

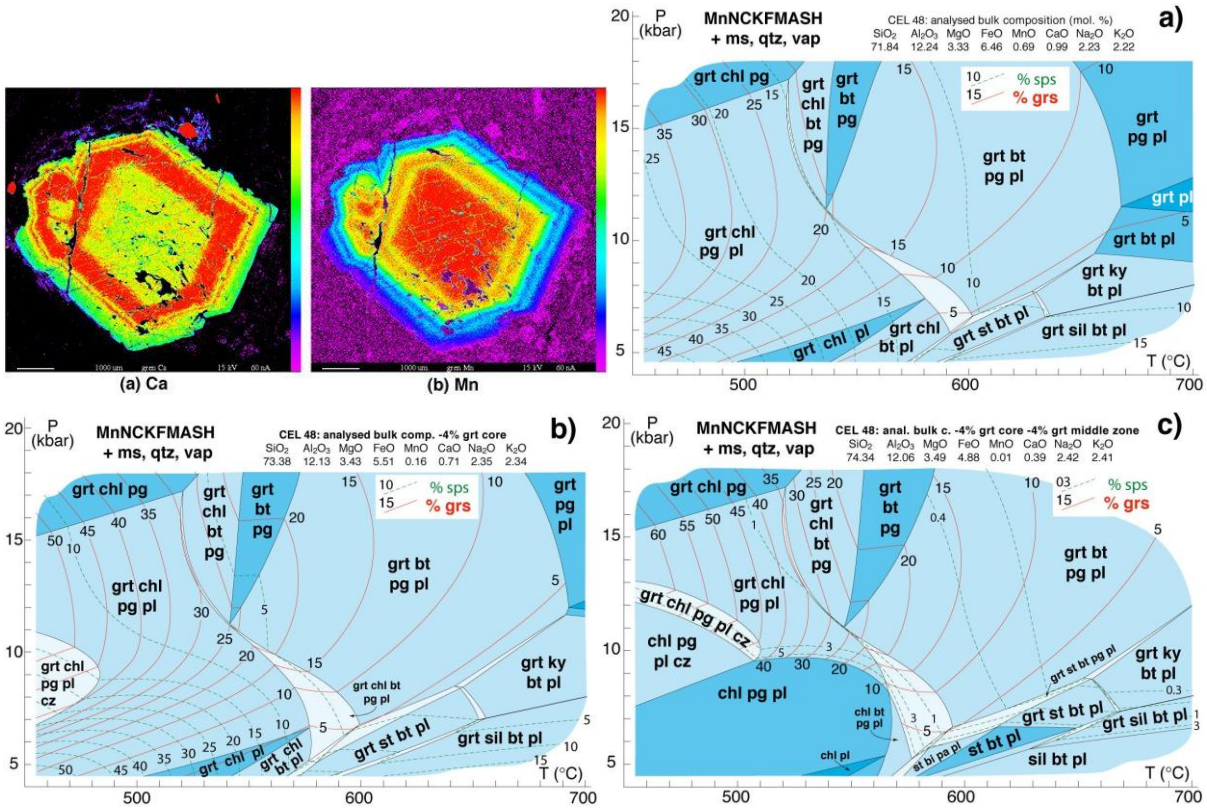


Fig. 15: X-ray maps of a strongly zoned garnet from the Champtoceaux complex (Armorican massif), and a series of P–T pseudosections contoured for garnet composition expressed as proportions (%) of spessartine (Mn) and grossular (Ca). a) is calculated for the analysed bulk composition. b) is for a composition where the garnet core (≈4% of the rock), inferred not in equilibrium with the crystallising matrix, was subtracted from the analysed bulk composition. The composition in c) is that of b) minus additional 4% of the garnet "high-Ca" middle zone. The main chemical effect is the decrease of the CaO and MnO content. The position of most fields remains unaffected, but the isopleths are significantly displaced. Garnet disappears at low pressures and temperatures.

Ferric iron

Iron commonly occurs in two oxidation states in rocks and minerals – the ferrous Fe^{2+} and the ferric Fe^{3+}. Metapelitic rocks form in general under relatively reducing conditions and calculations indicate that small to moderate amounts of Fe_2O_3 in typical metapelitic bulk compositions have little effect on silicate mineral equilibria in metapelites (e.g. White et al. 2000). The situation is different in metabasic rocks, where several minerals – in particular clinopyroxenes, clinoamphiboles and epidote – may incorporate significant amounts of Fe^{3+}, which has an important effect on their stability (e.g. Ballèvre et al. 2003; Warren and Waters 2006; Diener et al. 2007).

Since the formulation of satisfactory solid-solution models including ferric iron for amphiboles and pyroxenes (Dale et al. 2005; Diener et al. 2007; Green et al. 2007), it became clear that the amount of ferric iron in metabasic rocks needs to be taken into account. Unfortunately, because alteration may affect significantly the oxidation state, it became a common practice not to analyse specifically for FeO and Fe_2O_3 and deal with "total iron". Whereas this may be acceptable from the geochemical point of view, it clearly hinders a satisfactory understanding of phase relations and equilibration conditions of metamorphic, in particular metabasic rocks. In the absence of reliable data on the oxidation state of metabasic rocks, the amount of ferric iron can be estimated from the chemical composition and the mode of the minerals present (e.g. Ballèvre et al. 2003; Warren and Waters 2006). Nevertheless, in this case a supplementary uncertainty arises from the problematic estimation of the ferric iron content from microprobe analyses (e.g. Droop 1987). In this situation some authors relied on one of the rare systematic studies (Schilling et al. 1983), which suggested that ferric iron represents ca. 12% of total iron in the MORB-type rocks. Although this assumption lead to reasonable results (Diener et al. 2007; Pitra et al. 2010b), chemical analyses of unaltered metabasic rocks show that the amount of ferric iron may be significantly higher (e.g. up to ≈30% and ≈45% of total iron in the omphacite-bearing blueschists from Ile de Groix and Syros, respectively!), with non-negligible effects on the modelled phase relations (Fig. 16). It becomes clear that the amount of ferric iron in the bulk rock composition is a fundamental parameter that needs to be analysed systematically. Remains the problem of simple and accurate analysing of Fe^{3+} in individual minerals…

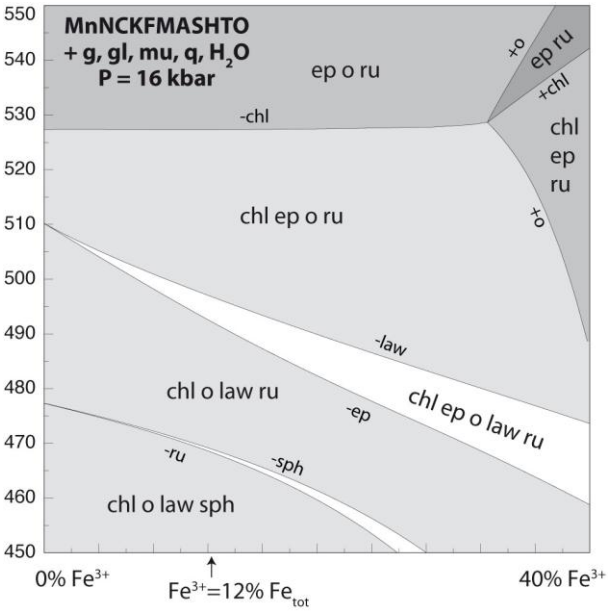


Fig. 16: T–X (temperature–composition) pseudosection calculated at 16 kbar for a blueschist (sample GAL1) from the island of Syros (Greece) by Lorraine Tual. The compositional vector corresponds to the variation of the proportion of the ferric out of the total iron. 12% corresponds to the amount of ferric iron reported by Schilling et al. (1983), 40% (extreme right) corresponds to the amount analysed in the sample. This amount seemed so unreasonably high that we started the calculations with 12% Fe^{3+}. The misfit between the model and the observations led us to reconsider this point. Note in particular the disappearance of omphacite (upper right corner) at high values of Fe^{3+}, in agreement with the (unusual in the sector) lack of omphacite in this sample.

Available H_2O

A vast majority of metamorphic reactions have a dehydration character and produce an H_2O-fluid when crossed upon heating, during the prograde evolution. Accordingly, most rocks are saturated in H_2O, which is then commonly considered in excess. Whereas this approach yields correct results in most cases, several exceptions merit to be stressed out:

1) *polycyclic evolution*: the above is only true if the metamorphosed rock is initially an unmetamorphosed or a low-grade hydrated rock. This is clearly not the case if metamorphism is imposed on a rock that suffered a previous metamorphic event and related dehydration.

2) *partial melting*: melting reactions are fluid-consuming (or fluid-absent) and the amount of available H_2O plays an important role for the phase relations beyond the solidus (e.g. Powell 1983; Powell and Downes 1990; White et al. 2001).

3) *retrograde evolution*: just as fluid is produced on the prograde path, it is consumed at the retrograde path. Accordingly, the amount of the available fluid at the onset of the retrograde evolution has important consequences for the phase relations upon cooling.

4) *subduction metamorphism*: metamorphism in subduction zones is characterised by low geothermal gradients (steep in a P–T diagram). Rocks following these gradients may cross some dehydration reactions in the 'wrong', H_2O-consuming direction. This is the case of the reactions involving lawsonite, which have a relatively 'flat' slope with lawsonite being stable at the high pressure, low temperature side. Consequently, rocks become H_2O-undersaturated with important implications for the phase relations and mineral assemblages encountered in such environments (e.g. Ballèvre et al. 2003; Clarke et al. 2006) (Fig. 17).

In all these cases the initial *available* amount of free H_2O-fluid needs to be estimated. It can be argued that for mechanical reasons free fluids in rocks can only be present at grain boundaries and limited intercrystalline spaces, the volume of which does not exceed 1-2 vol.%, but possibly as little as 0.1 vol. % (Thompson and Connolly 1990). The common procedure is to consider that the rock was "just fluid-saturated", i.e. containing some small, arbitrary amount of free H_2O-fluid at the moment just before crossing the fluid-consuming reactions.

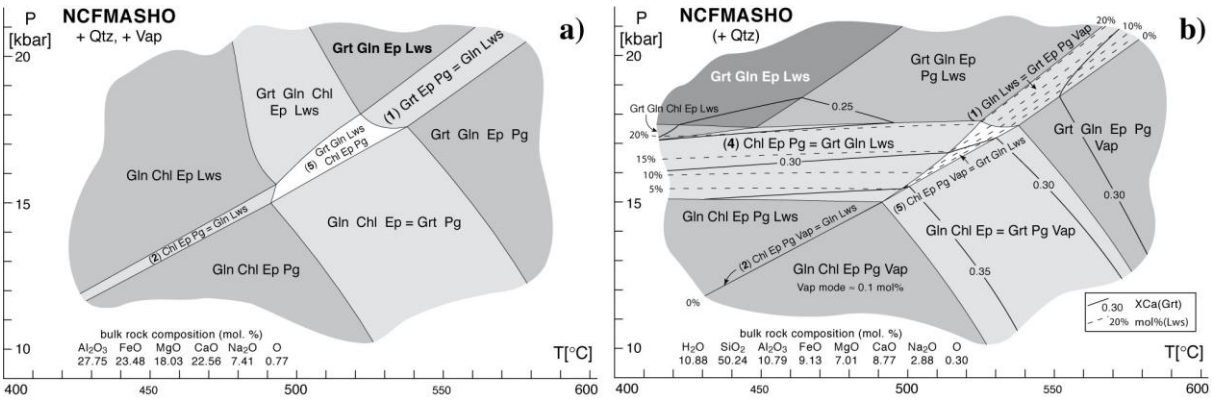


Fig. 17: P–T pseudosections calculated for a blueschist from Ile de Groix (Ballèvre et al. 2003). H_2O-fluid (Vap) is considered in excess in (a). The H_2O content was set so that about 0.1 mole % of free H_2O fluid is present in the stability field of Gln-Chl-Ep-Pg in (b). Whereas the fluid-saturated part of the diagrams is identical, significant differences exist in the H_2O-undersaturated, LT-HP part. Water undersaturation results in the extension of the fluid-absent equivalents of the high temperature fields towards lower temperatures and in the strongly pressure-dependent character of their boundaries.

Choosing the appropriate model system

Using simple model systems (like KFMASH for subsolidus pelitic rocks, or NCKFMASH for relations involving partial melting) has proven efficient in modelling first order observations and general processes (e.g. Powell and Holland 1990; Guiraud et al. 2001; White et al. 2001). When the goal is to understand the history of a particular rock, the situation is different. In theory, closer the model system is to the natural rock, better are the results. However, choosing a complex system implies longer calculation times and using more complex mixing models for solid-solution phases (see below), which may be a source of additional errors. Furthermore, even the sophisticated mixing models are commonly not complete enough to account for the inclusion of some minor components, like the potassium in amphiboles. Trying to take into account such minor components (e.g. calculating phase equilibria in metabasic rocks in a system including K_2O) may lead to spurious results.

As an example, the Ile de Groix lawsonite-bearing metabasic blueschists (Ballèvre et al. 2003) contain small amounts of K_2O. This is mostly present as the muscovite end-member in paragonite, which forms as the result of lawsonite destabilisation. The mineral assemblage comprises glaucophane, chlorite, epidote, paragonite, rutile and possibly garnet; muscovite is absent. In a pseudosection calculated recently in the system Na_2O-CaO-FeO-MgO-Al_2O_3-SiO_2-H_2O-TiO_2-Fe_2O_3 (NCFMASHTO) this assemblage is stable in a large domain between 11 and 18 kbar, 460-560 °C, in agreement with the calculations performed by Ballèvre et al. (2003) in NCFMASHO (and much simpler mixing models). It could be argued that the amount of muscovite in paragonite should be accounted for and calculations should be performed in a system containing K_2O. However, the addition of 0.5 mole% K_2O in the bulk composition and using the paragonite-muscovite solid solution (Coggon and Holland 2002) rather than pure paragonite, leads to results that strongly disagree with the observations: at the arbitrarily chosen conditions of 14 kbar, 510 °C, instead of the 'reasonable' gl-chl-ep-pa-ru assemblage in NCFMASHTO, modelling in NCKFMASHTO suggests glaucophane-omphacite-chlorite-muscovite-paragonite-rutile:

NCFMASHTO:

```
composition (from script)
   SiO2  Al2O3    CaO    MgO    FeO   Na2O   TiO2      O
 56.855  9.353  5.876 11.871      9  5.070  1.458  0.514
<================================================>
phases : gl, chl, ep, pa, ru, (q, fluid)

-------------------------------------------------------------------------
 P(kbar)     T(?C)    x(gl)    y(gl)    z(gl)    a(gl)    c(gl)    f(gl)   Q1(gl)   Q2(gl)
   14.00     510.0   0.3987   0.8286   0.9300  0.09510  0.06818  0.06097-0.007011   0.1034
                     x(chl)   y(chl)   Q(chl)    f(ep)    Q(ep)
                     0.4147   0.5117   0.4883  0.08189  0.08133

  mode       gl      chl       ep       pa       ru        q          G
        0.6444  0.09323   0.1696  0.02662  0.01327  0.05294 -588.86401
```

NCKFMASHTO:

```
composition
   SiO2  Al2O3    CaO    MgO    FeO    K2O   Na2O   TiO2      O
 56.574  9.307  5.847 11.812  8.955  0.498  5.045  1.451  0.511
<================================================>
phases : gl, o, chl, mu, par, ru, (q, fluid)

-------------------------------------------------------------------------
 P(kbar)     T(?C)    x(gl)    y(gl)    z(gl)    a(gl)    c(gl)    f(gl)   Q1(gl)   Q2(gl)
   14.00     510.0   0.3862   0.7892   0.9189  0.09358  0.07929  0.09239-0.007151  0.09846
                       x(o)     j(o)     f(o)     Q(o)   Qaf(o)   Qfm(o)
                     0.4100   0.4742   0.1427   0.3657  0.02345 -0.07755
                     x(chl)   y(chl)   Q(chl)    x(mu)    y(mu)   na(mu)    x(pa)    y(pa)   na(pa)
                     0.4069   0.5118   0.4882   0.3717   0.7754  0.09903   0.3717   0.9985   0.9715

  mode       gl        o      chl       mu      par       ru        q          G
        0.2130   0.3426   0.2010  0.05848  0.09817  0.01302  0.07370 -588.79523
```

Epidote is absent, omphacite is modelled to build up 34%, and muscovite 6% of the rock, whereas epidote is present and the latter two are absent from the sample. Although a further study is needed to fully understand this problem, it is clear that using a system "closer to the reality" is not helpful in this case.

Mixing models (a-x relations)

Numerical modelling of phase relations requires a *set of thermodynamic data* for mineral end-members (e.g. Berman 1988; Holland and Powell 1990; Holland and Powell 1998; Holland and Powell 2011), a description of the *activity-composition (a-x) relations* (the solid- (or liquid-) solution models or mixing models) and a *software* to perform the calculations (e.g. THERMOCALC, Powell et al. 1998). Accurate formulation of the mixing models for complex phases (like amphiboles, pyroxenes, phyllosilicates or silicate liquids) is a difficult task (e.g. White et al. 2001; Coggon and Holland 2002; Dale et al. 2005; Diener et al. 2007; Green et al. 2007). It commonly implies using end-members with poorly constrained thermodynamic data and requires fine tuning of the interaction parameters, many of which are not well known. A particular model may well work in a specific domain of P–T conditions and fail in others. More sophisticated models may fail, where simpler models gave satisfactory results (Fig. 18).

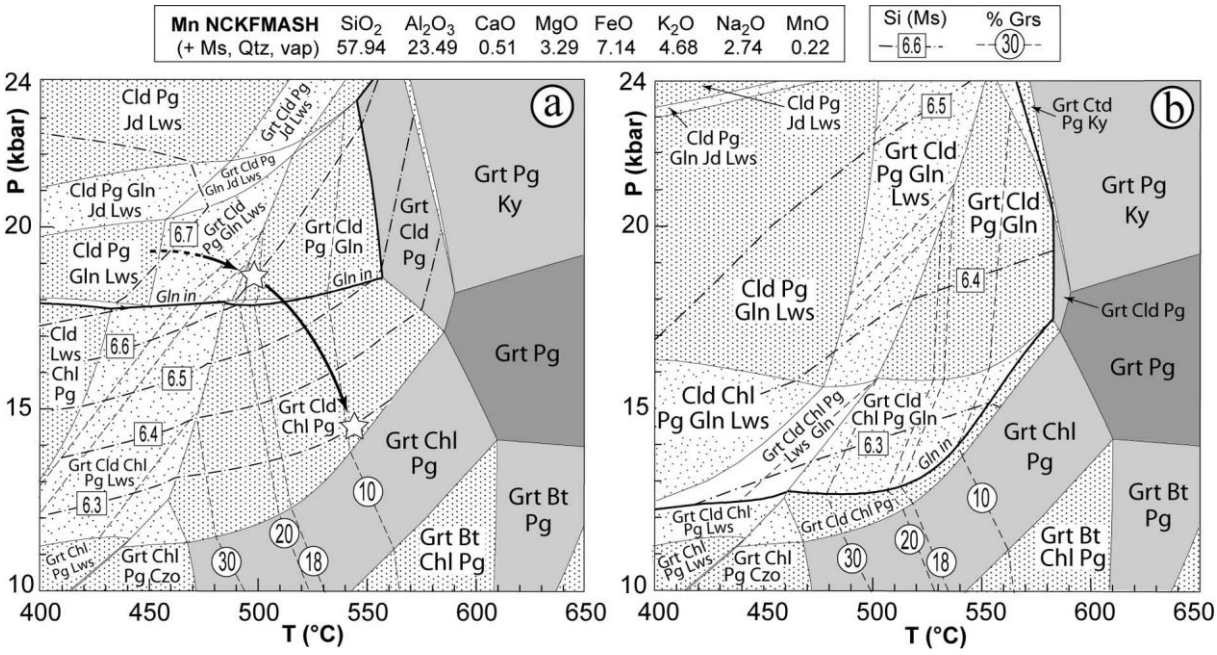


Fig. 18: P-T pseudosections calculated for a garnet+chloritoid+paragonite±chlorite -bearing metapelite from the Gran Paradiso massif (Le Bayon et al. 2006) (cf. Fig. 2; 7) using the glaucophane mixing model of (a) Wei *et al.* (2003) and (b) Dale *et al*. (2005) and contoured with compositional isopleths. Using the model of Wei *et al.* (2003) allows to account for the observations and propose a P-T evolution for the sample (a). On the other hand, the new model strongly extends the glaucophane stability field and results in a topology and position of the compositional isopleths incompatible with the observations (b).

Using the simple model of Wei *et al.* (2003), glaucophane appears by virtue of narrow di- and trivariant fields equivalent of the subisobaric NCKFMASH reaction Grt+Chl=Gln+Cld (+ Ms, Pg, Lws/Zo, Qtz, H_2O) at about 18 kbar. This reaction controls the development of glaucophane in most aluminous pelitic lithologies, including this sample, projecting between chloritoid and the Grt-Chl join in the AFM-type diagram (cf. Fig. 5 in Wei and Powell 2006). Consequently, moderate variations in bulk composition could

not explain the absence of glaucophane above this reaction. According to the position of the compositional isopleths, muscovite and garnet 2 cores would have equilibrated in the Grt-Cld-Pg-Gln field at PT conditions of about 18-20 kbar, 490-500°C. The small amount of glaucophane present at this stage (ca. 5%) could have easily reacted out during subsequent evolution, explaining its absence from the sample.

On the other hand, if glaucophane is modelled according to the more complex model of Dale *et al.* (2005), the NCKFMASH reaction Grt+Chl=Gln+Cld (+ Ms, Pg, Lws/Zo, Qtz, H_2O) has a strongly positive slope (10 kbar at 440°C, 18 kbar at 550°C) and the stability of glaucophane expands considerably towards low pressures. In consequence, the stability field of the main observed paragenesis Grt-Cld-Chl-Pg shrinks to merely a narrow band just beyond the Gln-in line. Moreover, the isopleths of Si(Ms) are shifted towards high pressures and there is no intersection between the isopleths corresponding to the composition of the cores of muscovite and that of garnet. Additionally, the highest values of Si-content measured in the muscovite cores and muscovite "inclusions" in garnet are modelled in the pseudosection only at extremely high pressures or low temperatures. In consequence, it is difficult to interpret the observed equilibrium relations in the framework of this diagram.

Finally, because the dataset has to be internally-consistent and the thermodynamic data for many end-members are not or poorly experimentally constrained, the generation of some data requires some hypotheses about the activity-composition relations to be made. Then, the dataset and the a-x relations used for phase equilibria modelling are not completely independent and care is needed for the user to choose the appropriate solid-solution model when using a particular dataset.

Available software

Two competing approaches (and related software) exist for constructing the pseudosections.

1) *Gibbs energy minimisation*. In this approach, the calculated diagram (P–T, P–X, T–X, …) is divided into a grid and Gibbs energy is minimised for each imaginable phase combination (within the selected system, using the selected mixing models for solution phases) at each point of the grid. At each point, the combination having the lowest Gibbs energy is declared the "stable" one and retained for the graphical output. The result is a juxtaposition of fields corresponding to the different phase assemblages. The field boundaries are not calculated, but interpolated between two points with non-identical phase assemblages. The software gives a (more or less elegant) graphical output of the result. Examples of software using this approach are **Perple_X** (Connolly 1990; Connolly and Petrini 2002) or **Theriak-Domino** (de Capitani and Brown 1987; de Capitani and Petrakakis 2010).

2) *Non-linear equation solver*. This approach uses the fundamental elegant fact that at the boundary between two fields with different phase assemblages, the Gibbs energies of both assemblages are identical and hence $\Delta G = 0$. Lines, instead of fields are calculated, by solving series of non-linear equations. It is the responsibility of the user to decide what equilibria should be calculated. The calculated lines need to be assembled manually in order to produce the desired phase diagram. **THERMOCALC** (Powell and Holland 1988; Powell et al. 1998) uses this approach.

The direct graphical output offered by the 'Gibbs energy minimisers' is appealing, as is the fact that the brain can rest while the software is performing the calculation. Nevertheless, this is also the danger of this approach. Far too often papers are submitted, and commonly accepted, which contain diagrams that contain serious errors, or are plainly wrong (perhaps is it wiser not to give references here). Indeed, although the calculations are performed automatically, a serious work is needed (beyond the petrographical analysis) in order to

choose the correct chemical system, appropriate mixing models, eliminate 'inappropriate' end-members, etc. (as outlined in the above sections).

Some of the errors (although rather minor) are related to the very principle of the method. In complex P–T regions, where many assemblages have closely similar energies, spurious results are locally obtained, related to the technical aspects of the calculation – here again the user input is needed (and sadly commonly lacking).

Despite all the drawbacks (time-consuming, not always user-friendly, capricious with starting guesses, no quick graphical output, …) the major advantage of THERMOCALC is the strong coherence between the software, the thermodynamic database and the development of mixing models, due to the long-term work of the group around Roger Powell and Tim Holland. Indeed, THERMOCALC is at present the only software capable of handling in an acceptable way phase relations in complex systems involving complex solid solutions (like the amphibole- and pyroxene-bearing metabasic rocks).

Finally, the intellectual implication required for using THERMOCALC makes the software more suitable for pedagogical purposes (which is not negligible for a lecturer) – the student can see what is happening and is required to think about the calculations that are to be performed, which leads to a much better understanding of the metamorphic systems.

To sum up, assuming an aware user, the rapidity and relative easiness of use make Perple_X and Theriak-Domino interesting alternatives for use in relatively simple systems (like the metapelitic rocks), in particular if a large range of various diagrams is to be calculated. THERMOCALC remains the best choice for calculating accurate phase diagrams in complex systems or with phases requiring complex mixing models. And this is also my choice…

Not only phase diagrams… avPT

Despite the general superiority of the phase diagram approach, 'geothermobarometry' can still yield useful results, in particular in the multi-equilibrium form (e.g. Powell and Holland 2008). THERMOCALC offers the possibility of performing multi-equilibrium geothermobarometric calculations – in the so-called "average PT", or "avPT", mode. Full details are discussed in Powell and Holland (1988; 1994). The major advantage of THERMOCALC in this domain is the realistic treatment of uncertainties and their propagation through the calculations. Using the χ^2 statistical test, THERMOCALC also allows to estimate the coherence of the input data used and, if needed, eliminate the inappropriate phases. Although the results may be disappointing (very large uncertainties in some high variance or incompletely equilibrated assemblages), at least this indicates that such rocks simply do not have the geothermobarometric potential expected and should not be used (although the phase diagram treatment may make them speak in some instances).

Finally, THERMOCALC-based average pressure-temperature calculations may give an idea of the activity of H_2O during metamorphism, by allowing to investigate the dependence of the uncertainties and the results of the χ^2 test ("fit") on $a H_2O$ (cf. Powell & Holland, 1988; 1994).

Two examples of using this method are given in the following section (Fig. 23, 26).

CASE STUDIES

High-pressure metamorphism and subduction zones

Subduction zones are privileged domains for studying plate tectonics, the dominant geological feature on present-day Earth. They make oceans disappear, allow the burial of rock into great depths and locally admit their exhumation. They may be precursors of the continental collision, which leads to the formation of orogens, and studying them presents the occasion to have an insight in the early stages of the mountain-building processes. These various aspects lead to a number of questions. What are the depths that the rocks may attain and still come back to the surface? What are the paths the rocks follow during the burial? How do they come back? How to explain the commonly observed intimate association of rocks that seem to have recorded significantly different metamorphic conditions? Did they record contrasting metamorphic evolutions? Is that only a problem of preservation? …

For a long time, the study of metamorphic rocks allowed and was focused on studying the conditions of the pressure/temperature peak and the retrograde evolution. This allowed to understand *exhumation processes* and mechanisms in various geodynamic contexts, but gave few answers on the early stages, on the paths the rocks follow during their burial. At present, the use of calculated phase diagrams in synergy with a careful study of the rocks' textures, revealing the succession of mineral crystallisations, preserved in certain porphyroblasts, and with the analysis of chemical growth zoning, allows the quantifying of *prograde P–T paths*. This allows to understand the thermal conditions of *burial* during the *early orogenic stages*. A couple of examples follow.

Lawsonite

Lawsonite is stable exclusively at low temperatures and high pressures and hence a mineral characteristic of subduction zones. Nevertheless, it is commonly absent, and if present, it is rarely fresh – in most cases it is replaced (pseudomorphed) by an association of secondary minerals. Blueschists from the island of Groix (Armorican massif) are known to locally display beautiful pseudomorphed lawsonite crystals. We have used these samples to study and understand the reactions that control the growth and destruction of lawsonite. The use of quantitative phase diagrams in this study (Ballèvre et al. 2003) led us to suggest that **lawsonite growth** was typically associated with the **prograde evolution** of the rocks. It formed through various continuous **hydration** reactions involving the consumption of primary chlorite and paragonite and this process was controlled by the initial amount of these phases. These lawsonite-forming reactions have a flat slope in the P–T diagram, which makes them suitable to **constrain the pressure** and hence the depth of burial of these rocks (Fig. 19).

This work has also demonstrated, through a detailed analysis of the microtextural relations, that **lawsonite growth was contemporaneous with the deformation** that resulted in the formation of the main foliation, and that this deformation ceased before lawsonite was pseudomorphed (cf. Fig. 11). The deformation can then be associated with the **prograde** part of the evolution of the Groix blueschists and is a marker of their **burial**. Lawsonite destruction took place during the onset of the exhumation of the blueschists and resulted in the formation of the epidote+chlorite+paragonite-bearing pseudomorphs.

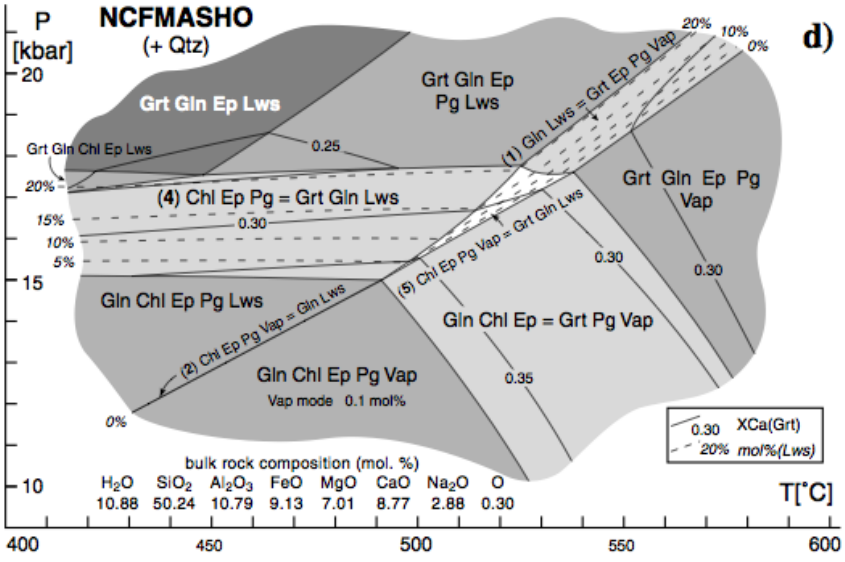


Fig. 19: P–T pseudosection calculated with THERMOCALC for the lawsonite-bearing blueschist from Ile de Groix. The phase diagram is calculated for a given bulk composition (indicated in the figure) and H_2O is *not* considered in excess. This results in *water undersaturation* in the HP-LT region (where lawsonite, a strongly hydrated phase, is stable) and in the very pressure-dependent character of the boundaries of the fluid-absent fields. The diagram displays the stability domains of the various phase assemblages. Nevertheless, the mineral *proportions* in the different fields may be highly variable. In this case, isopleths representing the mole proportion of the phases allow to visualise this phenomenon. In this case the isopleths of the amount of lawsonite are drawn. It is noticeable that whereas lawsonite may be theoretically stable at pressures as low as 11 kbar, it only appears *effectively* in significant proportions beyond the isobaric low-pressure limit of the field (4) Chl-Ep-Pg-Grt-Gln-Lws, at ca. 15 kbar. Furthermore, this assemblage (among others) is a reactional equilibrium. When the rock goes through, some phases are consumed (here essentially chlorite and paragonite) and others form (here mainly lawsonite). This is suggested by the non-traditional, 'reactional' writing of the assemblages: Chl-Ep-Pg=Grt-Gln-Lws.

The subject of associating different fabrics observed in the rocks with the prograde or retrograde part of their metamorphic evolution in a subduction zone has been explored in detail, from the structural point of view, during the PhD of Melody Philippon, recently accomplished at Géosciences Rennes and dedicated to the tectonics of the Cyclades. This year, during the post-doctoral stay of Melody in Rennes, we are collaborating on refining these results through a detailed microtextural analysis and calculated phase diagrams.

Associations of high-pressure and medium-pressure rocks

Eclogites and blueschists commonly occur as boudins within other rock types, such as felsic gneisses, various schists and metapelites, the metamorphic record of which does not commonly seem to testify to passing through the high-pressure domain. The common question is then whether the high-pressure rocks and the rocks enclosing them shared their entire *P-T* history (and the early stages have been selectively erased in some of them), just a part of it (and what is then the moment when they got together), or if their *P-T* histories are completely separate. Structural observations usually cannot help in answering this question. Such associations of eclogites, granitic orthogneisses and barrovian metapelites are present in the NE part of the Bohemian Massif. A detailed petrographical study associated with numerical modelling of phase equilibria, carried out when Pavla Štípská visited Géosciences Rennes as an invited researcher, led to publishing one of the first studies, where these relations were clearly shown (Štípská et al. 2006). In this region, it was possible to clearly

document the **prograde** and **retrograde** paths of both the eclogites and the barrovian metapelites (Fig. 20, 21).

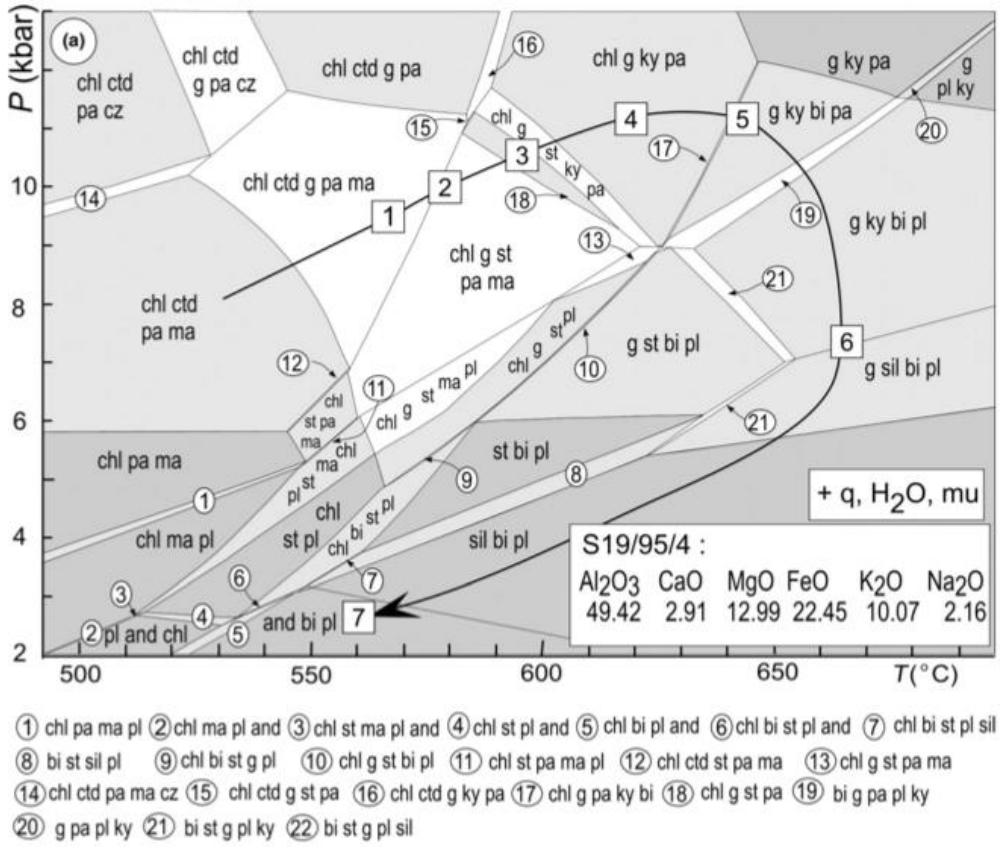


Fig. 20: P-T pseudosection for barrovian metapelites associated with eclogites in the NE Bohemian Massif (Štípská et al. 2006). Numbers in white squares indicate the equilibration conditions for the different successive assemblages preserved in the porphyroblasts. A nearly complete P–T path could be established and compared with the one calculated for the eclogites (Fig. 21).

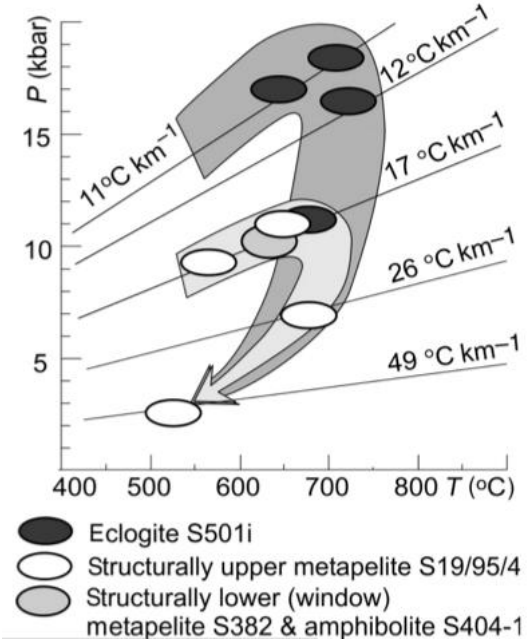


Fig. 21 Synthesis of P–T paths calculated for the metapelites and the eclogites from the NE Bohemian Massif. Prograde paths follow different geothermal gradients. Most of the retrograde evolution is common to both rock types.

This work has shown that the two rock types have followed **distinct prograde evolutions**, along **different geothermal gradients**. They minimum difference in peak pressures is ca. 6-7 kbar, corresponding to a difference in the burial depth of some 25 km. Both lithologies came together in depths of ca. 40 km (11 kbar) and shared the same retrograde evolution from this point on.

Although the geodynamic context, characterised by the metamorphic conditions and the geothermal gradients, is that of a continental accretionary prism rather than that of a subduction zone, the approach can clearly be exported into subduction zone contexts, where similar associations are frequently observed.

Inverted metamorphic sequences

A common feature of orogenic belts issued from continental collision is the presence of crustal-scale thrusts that superpose high-grade metamorphic units over lower-grade ones. The result is an inverted metamorphic zoning. Structural elements associated to these thrusts are commonly overprinted by later tectonic events, and inverted metamorphism is often **the only trace of continental collision** in old orogens. Despite numerous field-based studies and numerical models, the development of inverted metamorphic zoning, its preservation and exhumation remain controversial, although it is a key-point in understanding of orogenic processes. In particular, it is important to understand if the metamorphic inversion reflects, and to what extent, the transient **inversion of the geothermal gradient**. The combination of a petrological analysis and a detailed multi-method geochronological approach appears to be an efficient way to address this problem.

We have shown (Pitra et al. 2010a) that the Champtoceaux Complex (Armorican Massif) displays such an inverted metamorphic zoning (Fig. 22). The temperature of the syntectonic assemblages increases in a continuous way from <500°C to >650°C (Fig. 23), from the base of the sequence to the major thrust, marked by lenses of serpentinised peridotites, interpreted as remnants of an oceanic crust, at the base of a migmatitic unit. Yet, this temperature increase is not accompanied by a pressure gradient, which would be expected from a post-metamorphic inversion. No low-temperature shear zone has been observed within the inverted sequence. Finally, all the peak metamorphic assemblages are syn-kinematic. These observations led us to conclude that the inverted metamorphic gradient resulted form a **thermal perturbation**, induced by the **rapid emplacement of a hot nappe**, probably migmatitic, on colder rocks.

Ar-Ar geochronology allowed to show that metamorphism took place nearly simultaneously through the entire inverted sequence. But first of all, the similarity of the Rb-Sr and Ar-Ar ages on both sides of the major thrust testifies to a particularly efficient cooling of the whole sequence. This **rapid cooling**, attributable to a tectonic denudation, allowed the **preservation of the inverted metamorphic gradient**.

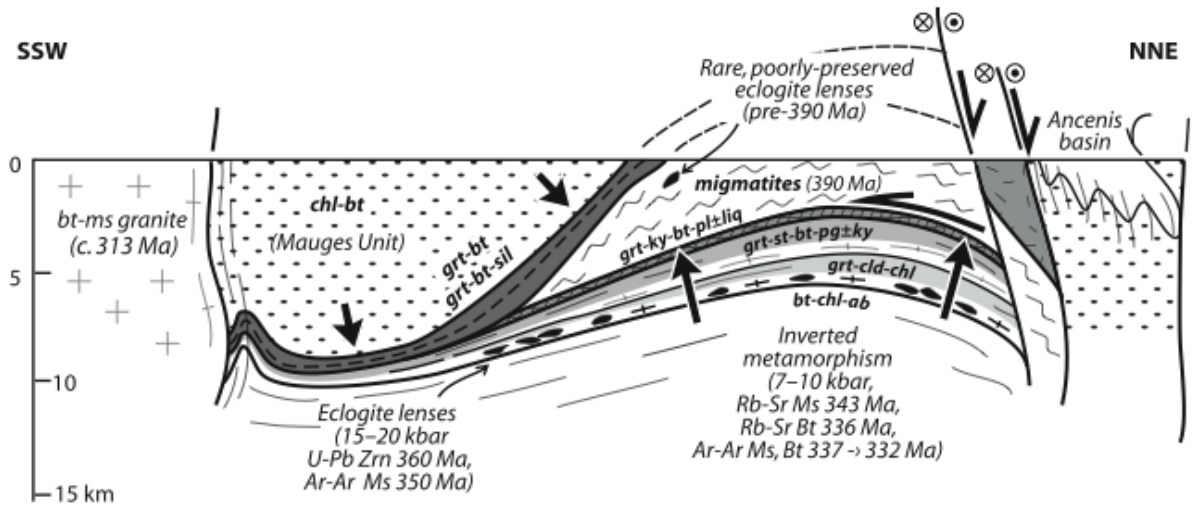


Fig. 22: Interpretative cross-section including the metamorphic history of the Champtoceaux area. Syn-kinematic assemblages associated with the main, nappe-forming, deformation, and post-dating the eclogite-facies event in the Champtoceaux Complex are indicated. Thick black arrows indicate increasing metamorphic grade. It thus appears that (i) an inverted metamorphic field gradient is found in the Champtoceaux Complex (with temperature increasing from the micaschists of the Parautochthon to the thrust contact with the Upper Allochthon migmatites), and (ii) a normal field gradient is found in the Upper Allochthon (in particular at the base of the Mauges Unit).

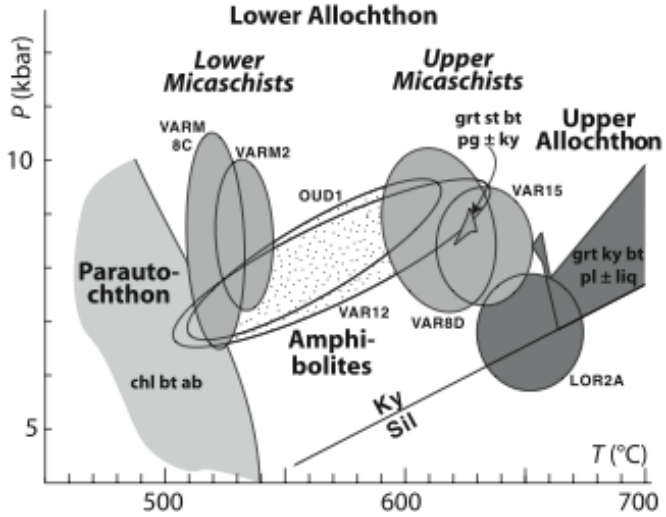


Fig. 23: Graphical representation of the results of the PT estimation. The ellipses correspond to the 1σ uncertainties on 'average PT' results as calculated by THERMOCALC. Other fields refer to the stability domains of the pertinent assemblages as deduced from the PT pseudosections (Pitra et al. 2010a).

Palaeoproterozoic homogeneous thickening

Whereas thrust-dominated crustal thickening is the dominant mechanism of Phanerozoic continental collisions (cf. inverted metamorphism), this has not always been the case. There is a general agreement that Archaean continental collisions were accommodated through homogeneous crustal thickening. However, a controversy exists about the character of the tectonics during Proterozoic times and especially during the Palaeoproterozoic. In the framework of a research project of Alain Kouamelan, invited researcher at Géosciences Rennes, I grasped the occasion to study the development of Palaeoproterozoic high-pressure mafic granulites in the Man shield (Ivory Coast). This gave me the opportunity to approach the continental collision in an entirely different context. Once again, the synergy of the structural, petrological and geochronological approach bore tasty fruit.

The eastern border of the Archaean Man shield in western Africa shows signs of important reworking during Palaeoproterozoic times. The presence of high-pressure granulites in this domain led several authors to suggest that Palaeoproterozoic tectonics was of "modern" type, dominated by flat-lying crustal thrusts. Our petrological study combined a detailed petrographical analysis with multi-equilibrium geothermobarometry (Fig. 26) and numerical modelling of phase equilibria at variable conditions of fluid saturation (Fig. 24, 25) (Pitra et al. 2010b). It allowed to suggest that the primary mineral assemblage of these mafic granulites, comprising garnet, diopside, red-brown amphibole and andesine equilibrated indeed at **high pressures and temperatures** – ca. 13 kbar, 850°C (Fig. 24). The subsequent development of spectacular symplectites forming reactional coronae (cf. Fig. 6) with orthopyroxene, green amphibole, diopside and bytownite around the primary phases could be understood through the use of P–T pseudosections calculated with a fixed amount of H_2O, leading to H_2O undersaturation at lower temperatures. The conditions of formation of these symplectites could be constrained to 7-8 kbar, <700°C (Fig. 25), suggesting an evolution dominated by **decompression at high temperatures**.

Geochronological data (Sm-Nd Grt-WR) confirmed the **Palaeoproterozoic age** of this event. Structural data, in particular the presence of the primary assemblages in the **systematically subvertical foliations**, led us to ascribe the formation of these granulites to a **homogeneous thickening** of the border of the Archaean craton, heated and softened by the accretion of a hot juvenile Palaeoproterozoic crust. Crustal shortening was mostly accommodated by a combination of transpressive shear zones and lateral crustal spreading rather than large-scale thrust systems (Fig. 27).

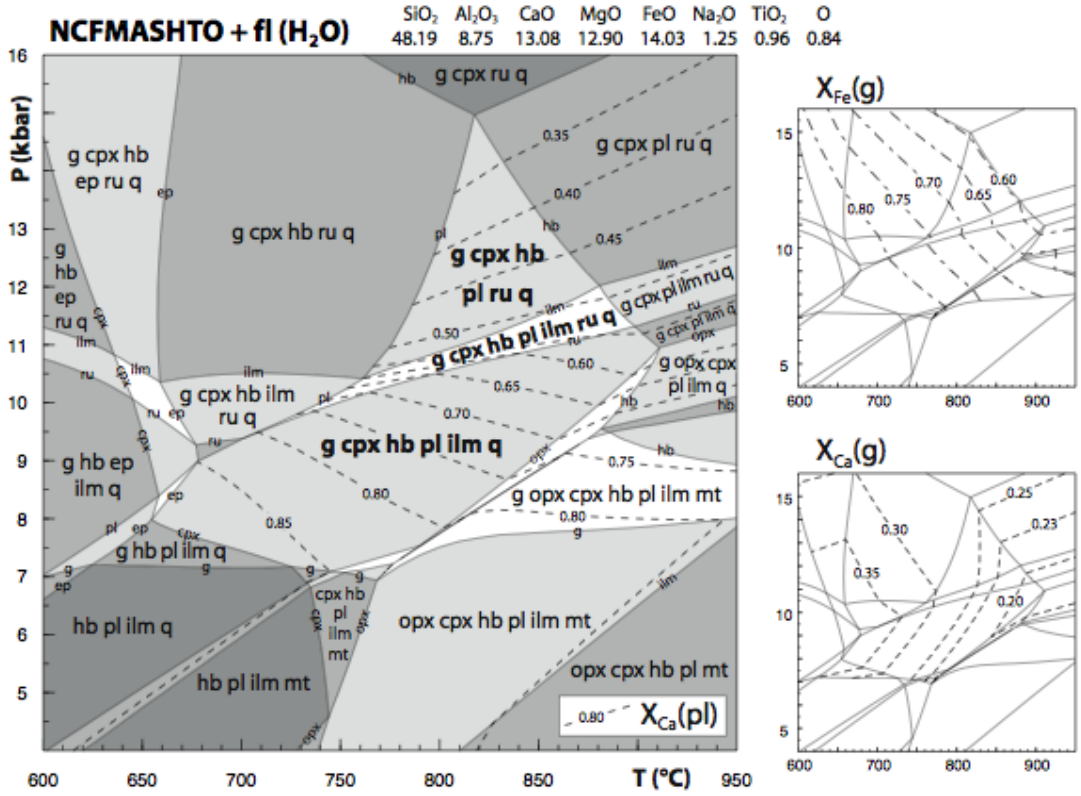


Fig. 24: P–T pseudosection calculated for the analysed composition of the mafic granulite with excess H_2O. The fields corresponding to the primary assemblage are highlighted. The position of the compositional isopleths corresponding to the composition of the primary minerals (X_{Fe} ratio and the grossular content of garnet, as well as the anorthite content of the primary plagioclase) allowed to further constrain the equilibration conditions (13 kbar, 850°C).

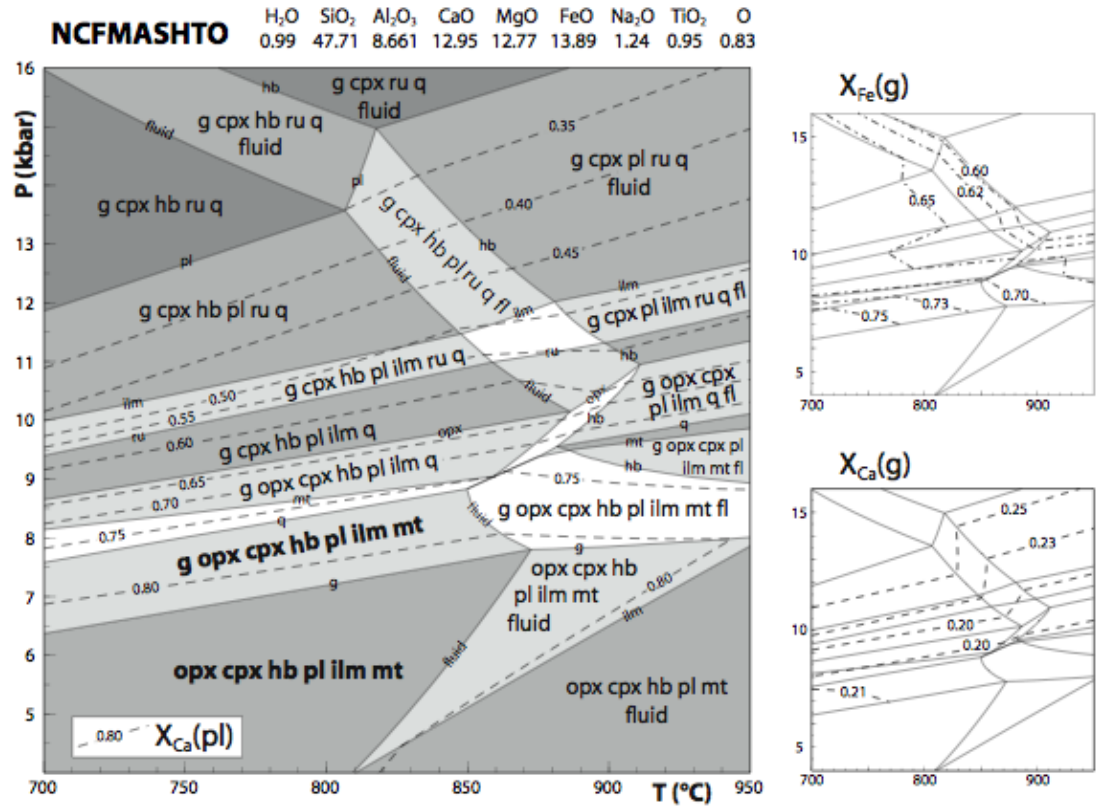


Fig. 25: P–T pseudosection calculated for the analysed composition of the mafic granulite with a **fixed amount of H_2O**. This amount was estimated so that at the primary *P-T* conditions, inferred from Figure 24,

the proportion of amphibole, the only hydrous solid phase in the system, corresponded to the observations (ca. 15 %) and there was a minimum proportion of free H_2O fluid phase in the rock (< 0.01 mole%). Compared to Figure 24, **water undersaturation** results in the extension of the fluid-absent equivalents of the high temperature fields towards lower temperatures and in the strongly pressure-dependent character of their boundaries (cf. Fig. 19). Orthopyroxene and magnetite are stable at pressures lower than about 10 kbar and 9 kbar, respectively. Quartz and garnet react out at pressures lower than ca. 8-9 kbar and 6-8 kbar, respectively. The isopleths of X_{Ca} in plagioclase (anorthite) and garnet (grossular) have a strongly pressure-dependent position and help to constrain the equilibration conditions of the secondary symplectitic assemblage (7-8 kbar, <700°C ; bold-labelled fields).

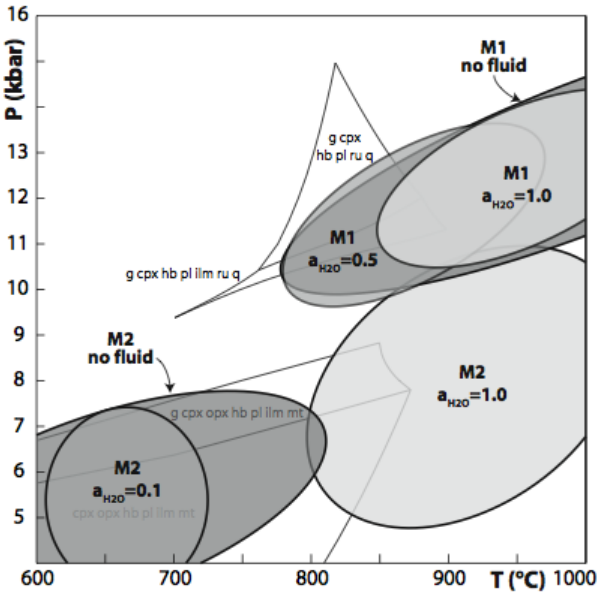


Fig. 26: Results of average *P-T* calculations (multi-equilibrium geothermobarometry) performed at different activities of H_2O. Uncertainty ellipses are drawn at the 2σ level. For comparison, contours of the stability fields of the primary (M1) and secondary (M2) assemblages, based on Figs. 24 and 25, are also represented. In spite of the large uncertainties, the diagram shows a good coherence of this approach with that based on phase diagrams, if the absence of fluids (low H_2O activity), suggested by the symplectitic character of the secondary textures, is taken into account.

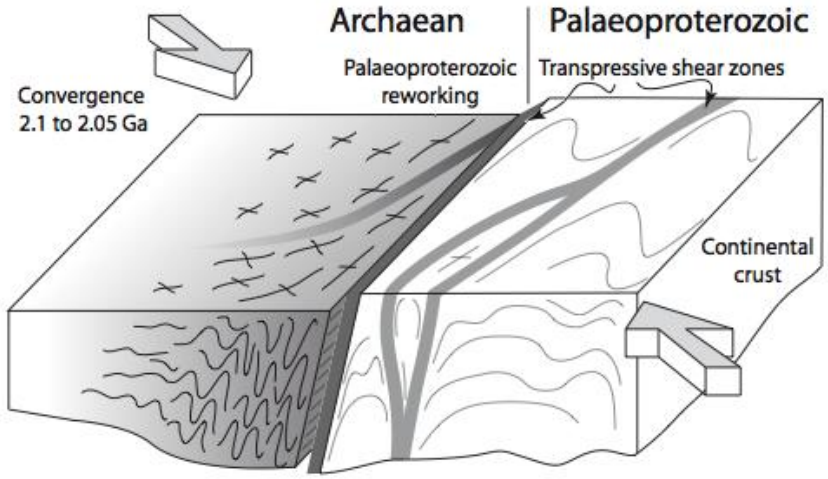


Fig. 27: Sketch illustrating the possible general framework of the collision between the hot juvenile Palaeoproterozoic crust and the Archaean craton and the reactivation of the latter, resulting in the formation of high-pressure granulites.

Metasomatic shear zones

Colleagues from Géosciences Rennes discovered thrust shear zones affecting granitoid orthogneisses at Ile d'Yeu (southern Armorican Massif) that recorded an important metasomatism (Sassier et al. 2006) resulting in the formation of peraluminous micaschists. This discovery awoke my desire to explore their potential for estimating the metamorphic conditions of these Variscan thrust zones.

This work first allowed to realise the extraordinary mineralogical richness of these shear zones. It lead to the discovery, in one of these shear zones, of a **cordierite–gedrite gneiss** bearing a rare magnesium-fluorine phosphate, **wagnerite** (Pitra et al. 2008). The petrographical analysis showed relic staurolite-bearing assemblage replaced by the cordierite+gedrite assemblage. The coarse-grained character, lacking any preferred orientation, of the secondary assemblage suggested that it was related to an **important fluid circulation** that continued after the major deformation ceased. The geochemical analysis, in particular the trace elements contents, indicated that this rock resulted from a **metasomatic alteration** of the neighbouring granitoid orthogneiss. The difficult, but crucial question had then to be asked, whether the observed paragenetic sequence resulted from a progressive change of the bulk chemical composition, or from an **evolution of the metamorphic conditions**. The use of calculated phase diagrams enabled to favour the second hypothesis (Figs. 28, 29).

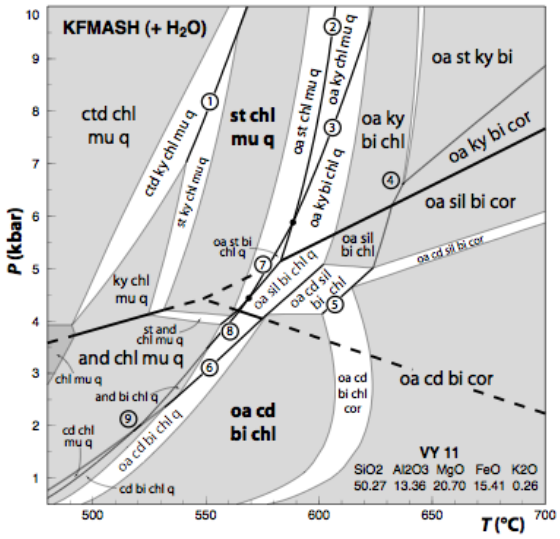


Fig. 28: P–T pseudosection for the analysed composition of the cordierite+gedrite (oa) gneiss. Both, the primary and the secondary assemblages are highlighted. The secondary assemblage (oa-cd-bi-chl) testifies to a post-deformational equilibration at <4 kbar, ≈550°C. Conversely, the primary, staurolite-bearing assemblage, contemporaneous with the formation of the shear zone, crystallised at higher pressures, indicating a barrovian-type metamorphism, characteristic of continental collision.

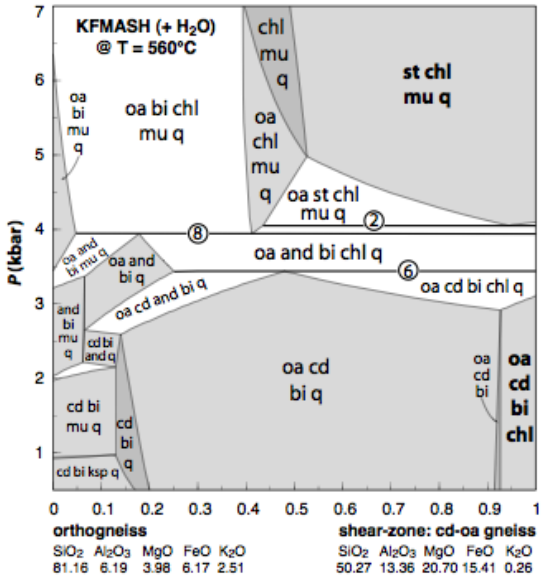


Fig. 29: Pressure-composition (P–X) pseudosection calculated at constant temperature. It displays the variation of mineral assemblages as a function of pressure and a compositional vector, which corresponds to a metasomatic evolution from the granitoid orthogneiss to the cordierite–gedrite gneiss. The staurolite-bearing assemblage can form in less metasomatosed rocks than the quartz-absent cordierite+gedrite one. Nevertheless, its stability is clearly restricted to higher pressures. This testifies to an evolution dominated by decompression of the shear zone.

The gneiss finished its transformation due to a circulation of post-kinematic fluids at low pressure (<4 kbar), but the major **thrust deformation developed under barrovian conditions**, at higher pressures. Work in progress aims now to add geochronological constraints to this interesting event, allowing to better understand the collision-related history of the southern Armorican Massif.

The unusual crystallisation of wagnerite resulted from the sequestration of calcium in plagioclase (although albitic), the crystallisation of which was related to a metasomatic enrichment of the rock in sodium. This prevented the crystallisation of the common phosphate, apatite.

In conclusion…

These examples of my recent research show that my work is based on a detailed petrological analysis and careful numerical modelling of phase diagrams, combined with a structural, geochemical and geochronological analysis. They also show that this approach, although apparently rather classic, may lead to major results and nourish a novel view of orogenic processes.

REFERENCES

Ballèvre, M., Pitra, P., and Bohn, M. (2003) Lawsonite growth in the epidote blueschists from the Ile de Groix (Armorican Massif, France): a potential geobarometer. Journal of Metamorphic Geology, 21(7), 723-735.

Berman, R.G. (1988) Internally-consistent thermodynamic data for minerals in the system Na2O-K2O-CaO-MgO-FeO-Fe2O3- Al2O3-SiO2-TiO2-H2O-CO2. Journal of Petrology, 29, 445–522.

---. (1991) Thermobarometry using multi-equilibrium calculations: a new technique with petrological applications. Canadian Mineralogist, 29, 833–855.

Caddick, M.J., Konopásek, J., and Thompson, A.B. (2010) Preservation of Garnet Growth Zoning and the Duration of Prograde Metamorphism. Journal of Petrology, 51(11), 2327-2347.

Carlson, W.D. and Rosenfeld, J.L. (1981) Optical determination of topotactic aragonite-calcite growth kinetics: metamorphic implications. Journal of Geology, 89, 615-638.

Clarke, G.L., Powell, R., and Fitzherbert, J.A. (2006) The lawsonite paradox: a comparison of field evidence and mineral equilibria modelling. Journal of Metamorphic Geology, 24(8), 715-725.

Coggon, R. and Holland, T.J.B. (2002) Mixing properties of phengitic micas and revised garnet-phengite thermobarometers. Journal of Metamorphic Geology, 20(7), 683-696.

Connolly, J.A.D. (1990) Multivariable phase diagrams: an algorithm based on generalized thermodynamics. American Journal of Science, 290, 666-718.

Connolly, J.A.D. and Petrini, K. (2002) An automated strategy for calculation of phase diagram sections and retrieval of rock properties as a function of physical conditions. Journal of Metamorphic Geology, 20, 697-708.

Dale, J., Powell, R., White, R.W., Elmer, F.L., and Holland, T.J.B. (2005) A thermodynamic model for Ca-Na clinoamphiboles in Na2O-CaO-FeO-MgO-Al2O3-SiO2-H2O-O for petrological calculations. Journal of Metamorphic Geology, 23(8), 771-791.

de Capitani, C. and Brown, T.H. (1987) The computation of chemical equilibrium in complex systems containing non-ideal solutions. Geochimica et Cosmochimica Acta, 51, 2639–2652.

de Capitani, C. and Petrakakis, K. (2010) The computation of equilibrium assemblage diagrams with Theriak/Domino software. American Mineralogist, 95(7), 1006-1016.

Diener, J.F.A., Powell, R., White, R.W., and Holland, T.J.B. (2007) A new thermodynamic model for clino- and orthoamphiboles in the system Na2O-CaO-FeO-MgO-Al2O3-SiO2-H2O-O. Journal of Metamorphic Geology, 25(6), 631-656.

Droop, G.T.R. (1987) A general equation for estimating Fe3+ concentrations in ferromagnesian silicates and oxides from microprobe analyses, using stoichiometric criteria. Mineralogical Magazine, 51, 431-435.
Enami, M., Suzuki, K., Liou, J.G., and Bird, D.K. (1993) Al–Fe3+ and F–OH substitutions in titanite and constraints on their P–T dependence. European Journal of Mineralogy, 5, 219 – 231.
Franz, G. and Spear, F.S. (1985) Aluminious titanite (sphene) from the Eclogite zone, south-central Tauern Window, Austria. Chemical Geology, 50, 33-46.
Green, E., Holland, T., and Powell, R. (2007) An order-disorder model for omphacitic pyroxenes in the system jadeite-diopside-hedenbergite-acmite, with applications to eclogitic rocks. American Mineralogist, 92, 1181-1189.
Guiraud, M., Holland, T., and Powell, R. (1990) Calculated mineral equilibria in the greenschist - blueschist - eclogite facies in Na2O-FeO-MgO-Al2O3-SiO2-H2O: Methods, results and geological applications. Contributions to Mineralogy and Petrology, 104, 85-98.
Guiraud, M. and Powell, R. (2006) P-V-T relationships and mineral equilibria in inclusions in minerals. Earth and Planetary Science Letters, 244(3-4), 683-694.
Guiraud, M., Powell, R., and Rebay, G. (2001) H_2O in metamorphism and unexpected behaviour in the preservation of metamorphic mineral assemblages. Journal of Metamorphic Geology, 19, 445– 454.
Harlov, D., Tropper, P., Seifert, W., Nijland, T., and Förster, H.-J. (2006) Formation of Al-rich titanite (CaTiSiO4O-CaAlSiO4OH) reaction rims on ilmenite in metamorphic rocks as a function of fH2O and fO2. Lithos, 88(1-4), 72-84.
Hensen, B.J. (1971) Theoretical phase relations involving garnet and cordierite in the system MgO-FeO-Al_2O_3-SiO_2. Contributions to Mineralogy and Petrology, 33, 191-214.
Holényi, K. and Annerstein, H. (1987) Iron in titanite: a Mössbauer-spectroscopy study. Canadian Mineralogist, 25, 429 – 433.
Holland, T. and Powell, R. (1990) An enlarged and updated internally consistent thermodynamic dataset with uncertainties and correlations : the system K_2O-Na_2O-CaO-MgO-MnO-FeO-Fe_2O_3-Al_2O_3-TiO_2-SiO_2-C-H_2-O). Journal of Metamorphic Geology, 8, 89-124.
Holland, T.J.B. and Powell, R. (1998) An internally consistent thermodynamic data set for phases of petrological interest. Journal of Metamorphic Geology, 16(3), 309-343.
---. (2011) An improved and extended internally consistent thermodynamic dataset for phases of petrological interest, involving a new equation of state for solids. Journal of Metamorphic Geology, 29(3), 333-383.
Hoschek, G. (2004) Comparison of calculated P-T pseudosections for a kyanite eclogite from the Tauern Window, Eastern Alps, Austria. European Journal of Mineralogy, 16, 59-72.
Hudson, N.F.C. (1980) Regional metamorphism of some Dalradian pelites in the Buchan Area, NE Scotland. Contributions to Mineralogy and Petrology, 73, 39-51.
Hudson, N.F.C. and Harte, B. (1985) K2O-poor, aluminous assemblages from the Buchan Dalradian, and the variety of orthoamphibole assemblages in aluminous bulk compositions in the amphibolite facies. American Journal of Science, 285, 224-266.
Johnson, T., Brown, M., Gibson, R., and Wing, B. (2004) Spinel-cordierite symplectites replacing andalusite: evidence for melt-assisted diapirism in the Bushveld Complex, South Africa. Journal of Metamorphic Geology, 22(6), 529-545.
Korzhinskii, D.S. (1959) Physicochemical Basis of the Analysis of the Paragenesis of Minerals. 142 p. Consultants Bureau, New York.
Le Bayon, B., Pitra, P., Ballèvre, M., and Bohn, M. (2006) Reconstructing P–T paths during continental collision using multi-stage garnet (Gran Paradiso nappe, Western Alps). Journal of Metamorphic Geology, 24(6), 477-496.
Lexa, O., Cosgrove, J.W., and Schulmann, K. (2004) Apparent shear-band geometry resulting from oblique fold sections. Journal of Structural Geology, 26, 155-161.
Li, Z.H., Gerya, T.V., and Burg, J.P. (2010) Influence of tectonic overpressure on P–T paths of HP–UHP rocks in continental collision zones: thermomechanical modelling. Journal of Metamorphic Geology, 28(3), 227-247.
Mancktelow, N.S. (2008) Tectonic pressure: Theoretical concepts and modelled examples. Lithos, 103(1-2), 149-177.
Marmo, B.A., Clarke, G.L., and Powell, R. (2002) Fractionation of bulk rock composition due to porphyroblast growth: effects on eclogite mineral equilibria, Pam Peninsula, New Caledonia. Journal of Metamorphic Geology, 20(1), 151-165.
Miyashiro, A. (1961) Evolution of Metamorphic Belts. Journal of Petrology, 2(3), 277-311.
---. (1973) Metamorphism and metamorphic belts. 492 p. Allen & Unwin, London.
Petrini, K. and Podladchikov, Y. (2000) Lithospheric pressure-depth relationship in compressive regions of thickened crust. Journal of Metamorphic Geology, 18(1), 67-78.

Philippon, M., Brun, J.-P., and Gueydan, F. (2009) Kinematic records of subduction and exhumation in the Ile de Groix blueschists (Hercynian belt; Western France). Journal of Structural Geology, 31, 1308-1321.
Pitra, P., Ballèvre, M., and Ruffet, G. (2010a) Inverted metamorphic field gradient towards a Variscan suture zone (Champtoceaux Complex, Armorican Massif, France). Journal of Metamorphic Geology, 28(2), 183-208.
Pitra, P., Boulvais, P., Antonoff, V., and Diot, H. (2008) Wagnerite in a cordierite-gedrite gneiss: Witness of long-term fluid-rock interaction in the continental crust (Ile d'Yeu, Armorican Massif, France). American Mineralogist, 93, 315-326.
Pitra, P. and de Waal, S.A. (2001) High-temperature, low-pressure metamorphism and development of prograde symplectites, Marble Hall Fragment, Bushveld Complex (South Africa). Journal of Metamorphic Geology, 19(3), 311-325.
Pitra, P., Kouamelan, A.N., Ballèvre, M., and Peucat, J.-J. (2010b) Palaeoproterozoic high-pressure granulite overprint of the Archean continental crust: evidence for homogeneous crustal thickening (Man Rise, Ivory Coast). Journal of Metamorphic Geology, 28(1), 41-58.
Powell, R. (1978) Equilibrium thermodynamics in petrology (An Introduction). 284 p. Harper & Row, London.
---. (1983) Fluids and melting under upper amphibolite facies conditions. Journal of the Geological Society, London, 140, 629-633.
Powell, R. and Downes, J. (1990) Garnet porphyroblast-bearing leucosomes in metapelites: mechanisms, phase diagrams, and an example from Borken Hill, Australia. In J.R. Ashworth and M. Brown, Eds., High Temperature Metamorphism and Crustal Anatexis, p. 105-123. The Mineralogical Society series, 2, Unwin Hyman, London.
Powell, R., Guiraud, M., and White, R.W. (2005) Truth and beauty in metamorphic phase equilibria: conjugate variables and phase diagrams. Canadian Mineralogist, 43(1), 21-33.
Powell, R. and Holland, T. (1990) Calculated mineral equilbria in the pelite system, KFMASH. American Mineralogist, 75, 367-380.
---. (1994) Optimal geothermometry and geobarometry. American Mineralogist, 79, 120-133.
Powell, R., Holland, T., and Worley, B. (1998) Calculating phase diagrams involving solid solutions via non-linear equations, with examples using THERMOCALC. Journal of Metamorphic Geology, 16(4), 577-588.
Powell, R. and Holland, T.J.B. (1985) An internally consistent dataset with uncertainties and correlations: 1. Methods and a worked example. Journal of Metamorphic Geology, 3, 327-342.
---. (1988) An internally consistent dataset with uncertainties and correlations: 3. Applications to geobarometry, worked examples and a computer program. Journal of Metamorphic Geology, 6, 173-204.
---. (2008) On thermobarometry. Journal of Metamorphic Geology, 26(2), 155-179.
Raimbourg, H. and Kimura, G. (2008) Non-lithostatic pressure in subduction zones. Earth and Planetary Science Letters, 274(3-4), 414-422.
Sassier, C., Boulvais, P., Gapais, D., Capdevila, R., and Diot, H. (2006) From granitoid to kyanite-bearing micaschist during fluid-assisted shearing (Ile d'Yeu, France). International Journal of Earth Sciences, 95, 2-18.
Schilling, J.G., Zajac, M., Evans, R., Johnston, T., White, W., Devine, J.D., and Kingsley, R. (1983) Petrologic and geochemical variations along the Mid-Atlantic Ridge from 27°N to 73°N. American Journal of Science, 283(6), 510–586.
Spear, F.S. (1993) Metamorphic phase equilibria and pressure-temperature-time paths. 799 p. Mineralogical Society of America, Washington.
Štípská, P., Pitra, P., and Powell, R. (2006) Separate or shared metamorphic histories of eclogites and surrounding rocks? An example from the Bohemian Massif. Journal of Metamorphic Geology, 24(3), 219-240.
Štípská, P. and Powell, R. (2005) Constraining the P-T path of a MORB-type eclogite using pseudosections, garnet zoning and garnet-clinopyroxene thermometry: an example from the Bohemian Massif. Journal of Metamorphic Geology, 23(8), 725-743.
Stüwe, K. (1997) Effective bulk composition changes due to cooling: a model predicting complexities in retrograde reaction textures. Contributions to Mineralogy and Petrology, 129(1), 43-52.
Stüwe, K. and Powell, R. (1995) PT paths from modal proportions: application to the Koralm Complex, Eastern Alps. Contributions to Mineralogy and Petrology, 119, 83-93.
Thompson, A.B. and Connolly, J.A.D. (1990) Metamorphic fluids and anomalous porosities in the lower crust. Tectonophysics, 1982, 47-55.
Thompson, A.B., Tracy, R.J., Lyttle, P.T., and Thompson Jr., J.B. (1977) Prograde reaction histories deduced from compositional zonation and mineral inclusions in garnet from the Gassetts schist, Vermont. American Journal of Science, 277, 1152-1167.
Thompson, J.B. (1959) Local equilibrium in metasomatic processes. In P.H. Abelson, Ed., Researches in Geochemistry, p. 427–457. Wiley, New York.

Tracy, R.J. (1982) Compositional zoning and inclusions in metamorphic minerals. In J.M. Ferry, Ed., Characterization of metamorphism through mineral equilibria, p. 355-397. Reviews in Mineralogy, 10, Mineralogical Society of America.

Tropper, P., Manning, C.E., and Essene, E.J. (2002) The substitution of Al and F in titanite at high pressure and temperature: experimental constraints on phase relations and solid solution properties. Journal of Petrology, 43, 1787 – 1814.

Ueno, T. (1999) REE-bearing sector-zoned lawsonite in the Sanbagawa pelitic schists of the eastern Kii Peninsula, central Japan. European Journal of Mineralogy, 11(6), 993-998.

Van Den Driessche, J. (1986) Structures d'enroulement et sens de cisaillement. Exemples et modèles. Comptes rendus de l'Académie des Sciences Paris, série II, 303(5), 413-418.

Van Den Driessche, J. and Brun, J.-P. (1987) Rolling structures at large shear strain. Journal of Structural Geology, 9(5-6), 691-704.

Vance, D. and Mahar, E. (1998) Pressure-temperature paths from P-T pseudosections and zoned garnets: potential, limitations and examples from the Zanskar Himalaya, NW India. Contributions to Mineralogy and Petrology, 132, 225-245.

Vernon, R.H. (1987) Oriented growth of sillimanite in andalusite, Placitas - Juan Tabo area, New Mexico, U.S.A. Canadian Journal of Earth Sciences, 24, 580-590.

Vernon, R.H., White, R.W., and Clarke, G.L. (2008) False metamorphic events inferred from misinterpretation of microstructural evidence and P-T data. Journal of Metamorphic Geology, 26(4), 437-449.

Warren, C.J. and Waters, D.J. (2006) Oxidized eclogites and garnet-blueschists from Oman: P-T path modelling in the NCFMASHO system. Journal of Metamorphic Geology, 24(9), 783-802.

Wei, C.J. and Powell, R. (2006) Calculated phase relations in the system NCKFMASH (Na2O-CaO-K2O-FeO-MgO-Al2O3-SiO2-H2O) for high-pressure metapelites. Journal of Petrology, 47(2), 385-408.

White, R.W. and Powell, R. (2002) Melt loss and the preservation of granulite facies mineral assemblages. Journal of Metamorphic Geology, 20(7), 621-632.

White, R.W., Powell, R., and Holland, T.J.B. (2001) Calculation of partial melting equilibria in the system Na_2O-CaO-K_2O-FeO-MgO-Al_2O_3-SiO_2-H_2O (NCKFMASH). Journal of Metamorphic Geology, 19(2), 139-153.

White, R.W., Powell, R., Holland, T.J.B., and Worley, B.A. (2000) The effect of TiO2 and Fe2O3 on metapelitic assemblages at greenschist and amphibolite facies conditions: mineral equilibria calculations in the system K2O-FeO-MgO-Al2O3-SiO2-H2O-TiO2-Fe2O3. Journal of Metamorphic Geology, 18(5), 497-511.

Winter, J.D. (2001) An introduction to igneous and metamorphic petrology. 697 p. Prentice Hall, Upper Saddle River, New Jersey.

Worley, B. and Powell, R. (1998) Singularities in NCKFMASH (Na2O-CaO-K2O-FeO-MgO-Al2O3-SiO2-H2O). Journal of Metamorphic Geology, 16(2), 169-188.

PERSPECTIVES

In coherence with my past research activity, my projects for the years to come remain centred on the use of numerical modelling of phase equilibria for a better understanding of orogenic processes. Nevertheless, I aim to enrich this approach by a collaborative association of numerical modelling of geodynamic processes, in particular through collaboration with Philippe Yamato, recently recruited at Geosciences Rennes. My plans are centred on three axes, two fundamental, and the third one slightly more technical:

- metamorphism and shear zones

- development of inverted metamorphic sequences

- application statistical methods

These aspects are presented in more detail below.

Metamorphism and shear zones: from the field to the model

A PhD project

Understanding the liberation and circulation of metamorphic fluids is indispensable for understanding geological processes. They take part in most metamorphic reaction and are commonly associated with zones of localised deformation. Through their rheological impact, they control the emplacement of tectonic units in mountain belts, but also the style of deformation.

It would be interesting to study shear zones at various scales (from the millimetre to the kilometre), in some selected target regions (Alps, Norway, Variscan belt), from the point of view of metamorphic transformations and evaluate the interactions with deformation, fluid circulation and a possible associated metasomatism. Following a careful field description, thermodynamic modelling of phase equilibria would be associated with thermomechanical models in order to understand the behaviour of shear zones during orogeny. What do they record (burial, exhumation,…), what are the relations with the neighbouring undeformed rocks?

Associating field work, metamorphic petrology and numerical modelling is expected to produce novel results in the understanding of the rheological behaviour of the lithosphere and the impact of the geodynamics of convergent zones.

With P. Yamato we plan to propose this problem as a PhD subject this year.

Thermodynamic modelling of fluid-rock interactions: example of the magnesian metasomatism

What follows is a part of a scientific project proposed to the INSU (CNRS) with Philippe Goncalves and Didier Marquer (Besançon)

Crystallisation of metamorphic minerals is achieved by diffusion of chemical components between the minerals and the percolating fluids and liquids. The driving force is the presence of chemical potential gradients. Quantitative phase diagrams using chemical potentials as variables are known and occasionally used for deciphering the evolution of metamorphic rocks since the pioneering work of Korzhinskii (1959). However, only the recent development of software tools for the calculation of thermodynamic phase equilibria (THERMOCALC, Perple_X) made it possible to study the *quantitative* relations between metamorphic crystallisations and transport of chemical constituents (e.g. through diffusion or fluid circulation), and to understand its causes through the evolution of chemical potential gradients (e.g. White et al., 2008). The use of equilibrium thermodynamics (the underlying principle of the above software) may seem unadapted for this kind of problem. Yet, at each moment of the metasomatic or reactional process, the systems tend to achieve *local equilibria* (e.g. Korzhinskii, 1959; White et al., 2008, Pitra et al., 2010), which can be addressed via this approach. Moreover, open systems may tend to achieve equilibrium even more rapidly and easily than closed ones, since they are commonly characterised by the presence of fluids that facilitate diffusion, transport of elements on grain boundaries and hence equilibration.

This problem is particularly interesting in metasomatic systems. In classic metasomatic systems (e.g. skarns) material transport controls the types of mineral composition (metasomatic fronts). However, thermodynamic modelling suggests that in some cases metamorphic recrystallisations in deformed rocks may induce the flux of metasomatising elements (Fig. 1).

In this project, we want to apply thermodynamic modelling on local equilibria in open systems in order to quantify the physical and chemical characteristics (P-T-X-µ) of the processes involved in fluid-rock interactions. Our goal is to get an insight into the respective roles of **mass-transfer and metamorphic crystallisations** during large-scale fluid circulations (chemical mass-transfer enhanced by metamorphic reactions vs. metamorphic crystallisations enhanced by chemical mass-transfer) (Oliot et al., 2010). This subject presents a fundamental scientific interest for understanding the processes of formation of metamorphic rocks. However, since many ore deposits are of metasomatic origin, the project has the potential to enhance our understanding of the formation of some of these deposits.

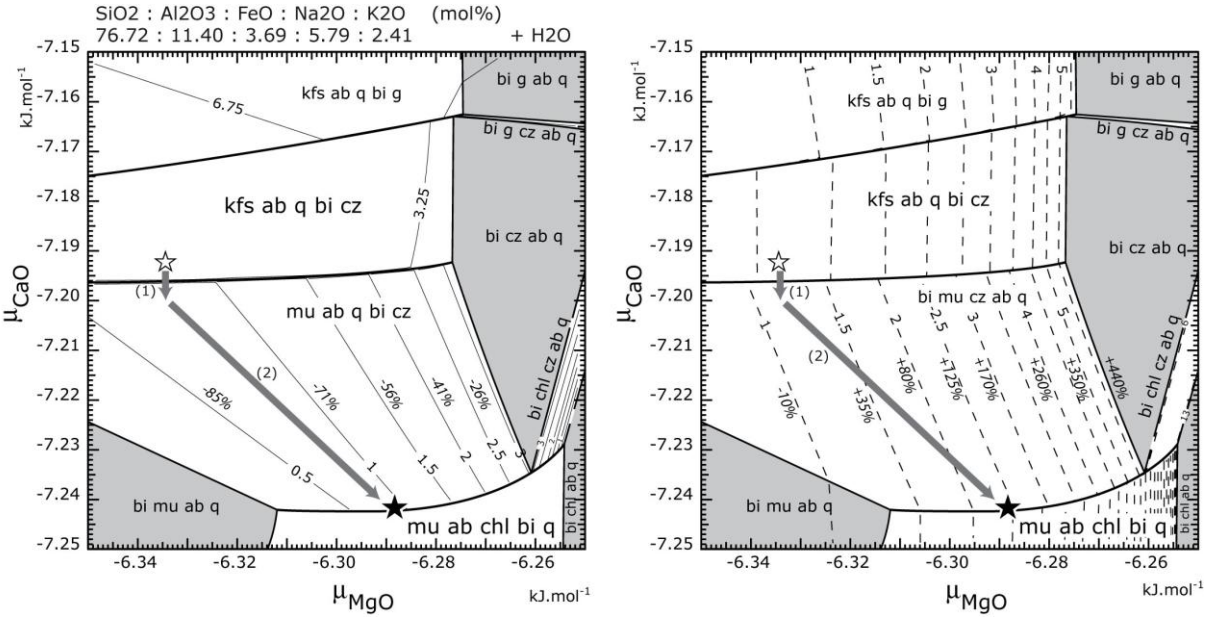


Fig. 1: Chemical potential (μ-μ) diagrams allow an original and quantitative view on the *causes* and *effects* of chemical mass-transfer in rocks. Here, we have calculated μ_{MgO}–μ_{CaO} pseudosections (where MgO and CaO are mobile constituents) in order to understand the mineralogical and chemical changes in shear zones affecting a granodiorite from the Aar massif (Swiss Central Alps). Deformation is accompanied by important gains in Mg and leaching of Ca (and Na). Such a correlation (MgO / CaO±Na_2O) has been observed in various other contexts and lithologies and merits an explanation.

During the deformation of the granodiorite, first magmatic plagioclase reacts and produces albite + epidote. An extensive crystallisation of muscovite, at the expense of K-feldspar, follows. Locally, chlorite crystallises in most deformed domains.

In the above diagrams, the stability of various mineral assemblages may be viewed as a function of chemical potentials μ_{MgO} and μ_{CaO}, and by extension as a function of the chemical composition of the system. The white and black stars correspond to the compositions of the protolith and the ultramylonite, respectively. Thin full (a) and dashed (b) lines represent the isopleths of the content of CaO (a) and MgO (b), respectively, in weight %. Numbers in italic represent the amount of gain or loss of the given element (oxide) compared to the protolith.

The diagrams show that

(1) only a decrease in the chemical potential of CaO (≈ loss of CaO) can lead to the destabilisation of K-feldspar (kfs) into muscovite (mu) in the presence of albite, epidote (clinozoisite) biotite and quartz. The chemical potential of MgO may remain stable (vertical arrow). The total loss of CaO, controlled by the reaction of destabilisation of kfs is of 76% (from 3.39 to 0.79 wt%), which is compatible with the analysed contents of weakly deformed orthogneisses (protoliths) and the ultramylonites.

(2) Following the complete disappearance of K-feldspar, the consumption of epidote and crystallisation of chlorite (black star) imply an evolution of chemical potentials of CaO and MgO along a path represented by the long grey arrow. Figure 1b shows that the recrystallisation in the shear zone is characterised by a decrease of the chemical potential of CaO, whereas the *quantity* of CaO remains *constant*. This implies and absolute gain of MgO of 125% (from 1.11 to 2.50 wt%).

In other words, the nature and quantity of mass-transfer seems to be controlled by thermodynamic equilibria.

The cause of the initial loss of CaO remains to be explained. The answer lies possibly in the composition of the metamorphic fluid.

Why magnesian metasomatism?

The unusual concentration of MgO in come crustal rocks is attributed either to unusual protoliths (evaporites, alterites, etc.), either to the chemical modification of "ordinary" protoliths (Fig. 2). This is then called the "**magnesian metasomatism**" This enrichment is commonly attributed to intense fluid circulation localised along crustal discontinuities.

Whereas the *effects* of such processes are evident, the *causes*, as well as the *sources* and *pathways* of the magnesium-rich fluids remains poorly known. Whereas in some cases local redistribution may be invoked, in other cases the quantity of the mass-transfer suggests the involvement of an external source. There are two major sources of magnesium advected into the continental crust – the Earth's mantle and the ocean. To deal with Mg-metasomatism means then addressing the general problem of large scale exchanges between the major terrestrial reservoirs (mantle–ocean–crust) through fluid circulations.

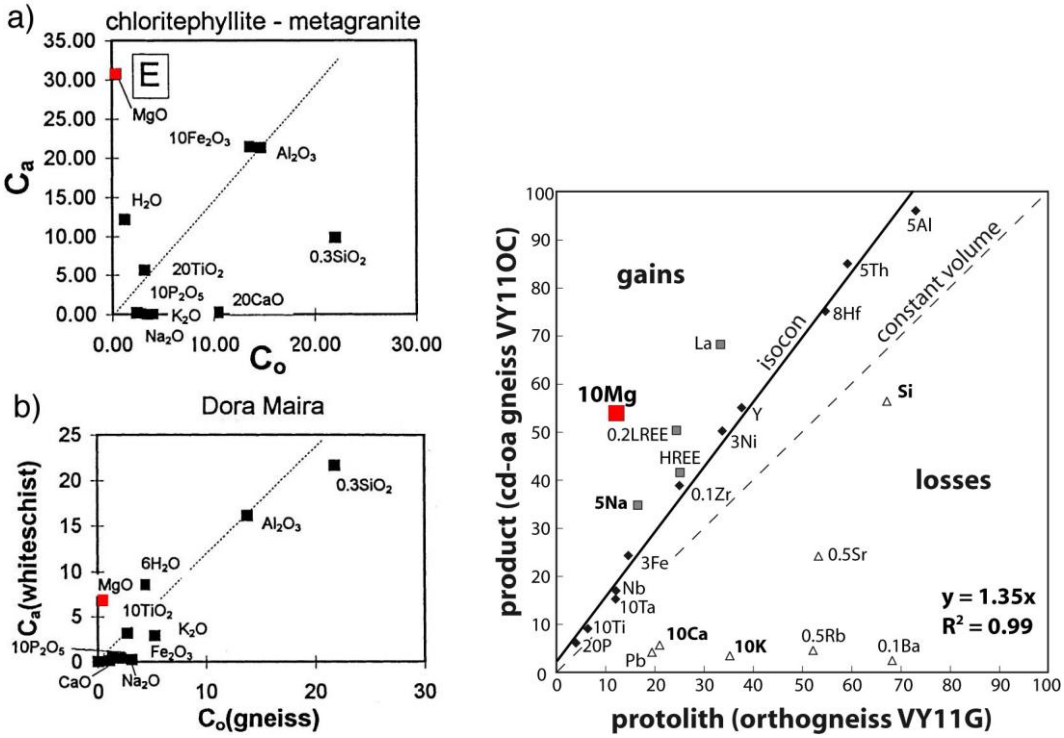


Fig. 2: Isocon diagrams (Grant diagrams) allow the comparison of the elementary concentrations between metasomatic rocks and their protoliths. a-b) Leucophyllites (Eastern Alps) and whiteschists (Western Alps), respectively, compared to their metagranitic protoliths (Demény et al., 1997). Despite the different structural and metamorphic context of both zones, the common feature is the strong enrichment in Mg and leaching of Ca and Na. c) Gedrite-cordierite gneiss in a shear zone of Ile d'Yeu (French Armorican Massif), cross-cutting a granitic orthogneiss (Pitra et al., 2008). Again, a strong enrichment in Mg and loss of Ca can be observed (cf. Fig. 1). Despite a different geodynamic context, different ages and metamorphic conditions, there are striking geochemical similarities between these three examples.

The deformation of rocks leads to the development of shear zone systems. Such discontinuities may localise the flow of fluids of superficial, metamorphic or magmatic origin. These fluids interact with the rocks, dissolve some elements and precipitate others, depending on the physico-chemical conditions of the interaction. These processes are accompanied by

the crystallisation of numerous metamorphic minerals, which can be used to constrain the physical and chemical conditions of the interaction as well as its timing and P-T-t-d paths.

Numerous examples of shear zones show evidence of mass-transfer (e.g. Rossi, 2005). These discontinuities within the continental crust display commonly strong Mg-enrichments under different metamorphic conditions (e.g. Marquer & Burkhard, 1992 and references therein). Such lithologies are particularly reactive during metamorphism and may yield precious information on orogenic evolution, unavailable from other rock types (Fig. 3). The Alpine whiteschists, possibly an ultimate end-member of Mg-metasomatism, are a well-known example (e.g. Chopin et al., 1991; Schertl & Schreyer, 2008).

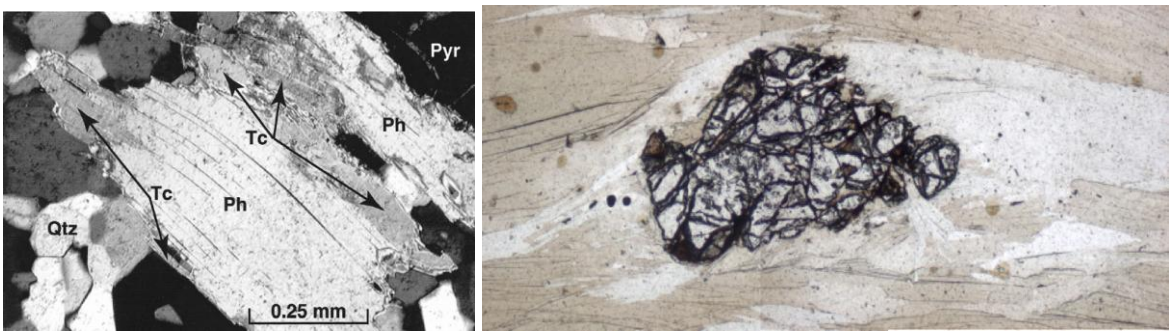


Fig. 3: Magnesian lithologies display unusual mineral compositions that have a scientific (e.g. deciphering tectonometamorphic evolution of orogens), but also economic interest (magnesian minerals used as lubricants, refractory materials, etc.). (a) Phengite+talc+pyrope+quartz-bearing whiteschist (Ferraris et al., 2000): in the Alps, these ultra-high pressure rocks preserve information of continental subduction. (b) Phlogopie+Mg-chlorite+corundum-bearing micaschist of metasomatic origin from a shear zone on Ile d'Yeu. This rock yielded unexpected information on PT conditions and the age of the Variscan compression in this part of the Armorican Massif (Pitra & Antonoff, 2007; Donguy, 2008).

Moreover, datable minerals (hydrothermal zircon, monazite, xenotime, rutile, …) commonly crystallise during deformation and associated fluid-rock interactions (e.g. Schaltegger et al., 2005; Pelleter et al., 2007). They can be used to constrain the moment of the interaction, and possibly also its duration.

Nevertheless, despite the interesting nature of these rocks, there is no consensus concerning their origin. Different authors suggest the metamorphism of evaporites (e.g. Schreyer, 1977), metamorphism of superficially altered granites (Pawlig & Baumgartner, 2001), syn-metamorphic metasomatism (Demény et al., 1997; Compagnoni & Hirajima, 2001), or interaction with anatectic liquids and fluids (Philippot et al., 1995). The problem is not solved so far.

Such zones of Mg-enrichment, commonly associated with intense fluid circulations in open systems, are then an ideal target to tackle the problem of the relations between mass-transfer and metamorphic crystallisations. They also allow addressing other important questions, such as the character of the fluids involved or the stability of mineral assemblages during fluid-rock interactions.

However, rather than address directly the most evolved products of these processes, like the whiteschists, we propose to study *small* shear zones, which comprise magnesian lithologies and develop at the expense of relatively simple rocks.

We have started this project in 2009 through a structural, geochemical and petrological study of metasomatic Mg-rich shear zones affecting granitoid orthogneisses of the Leventina and Simano nappes in Val Leventina (Swiss Central Alps; Fig. 4). There, shear zones develop within metagranites of homogeneous texture and composition and display progressive metasomatic transformations.

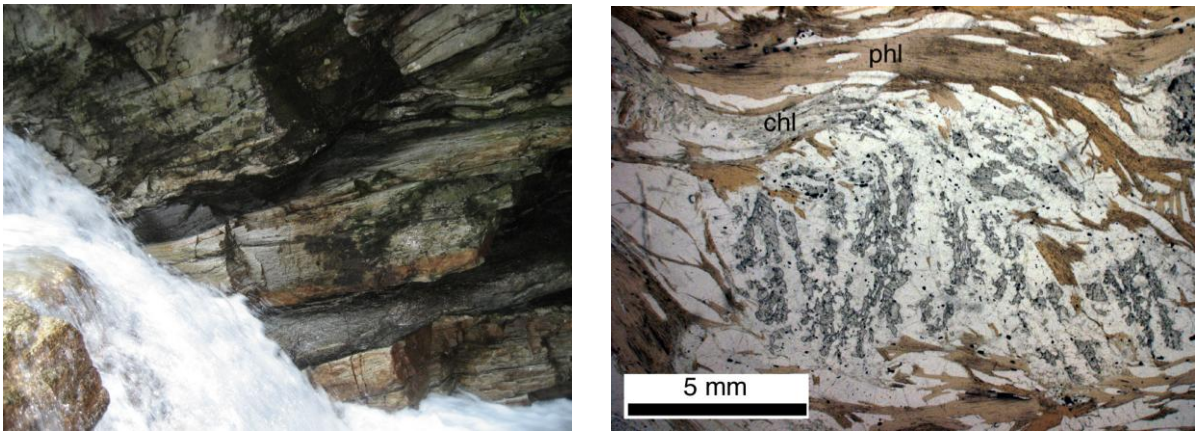


Fig. 4 : (a) Shear zones within granitoid orthogneisses in Val d'Ambra (Val Leventina, Ticino, Switzerland). (b) An example of a Mg-rich rock from one of the shear zones on (a), collected during the 2009 mission. A syntectonic kyanite porphyroblast (with numerous inclusions of rutile), partly replaced by cordierite a wrapped by a phlogopite+Mg-chlorite-bearing foliation.

Subsequently, in July 2010 we have collected samples from similar Mg-rich shear zones, also affecting granitoid orthogneisses, and geographically associated with talc and magnesite deposits in the Veporic unit (Western Carpathians, Central Slovakia; Kováčik, 1996). Finally, we shall revisit samples from an equivalent setting that we have studied on Ile d'Yeu (French Armorican Massif). Consequently, we have a collection of samples from metasomatic Mg-rich shear zones developed at the expense of granitoid orthogneisses from three distant localities, of different tectonic and metamorphic settings, which display different mineral compositions, but striking chemical similarities. Geochemical data collected from the shear zones in Val Leventina and those from Ile d'Yeu suggest that the magnesian lithologies do indeed originate from the granitoid orthogneisses and do not have an "exotic" protolith (Fig. 5).

Although these strongly magnesian rocks are relatively rare, they are present in small quantities, as horizons or lenses, in virtually all mountain belts. Beyond their scientific significance, their mineral composition makes them interesting also from the economic point of view (e.g. Moine et al., 1989; Nemeth et al., 2004; Robb, 2005):

1) They may be exploited as mineral deposits (talc, magnesite, chlorite, …).

2) They are frequently accompanied by other ore deposits (U, Au, Zn, VMS, …) and are, as such, used as indicators during mining exploration (e.g. Rouhunkoski, 1968; Mernagh et al., 1998; Galley et al., 2007a, 2007b).

We expect that this study should improve the existing models of Mg-metasomatism used in exploration.

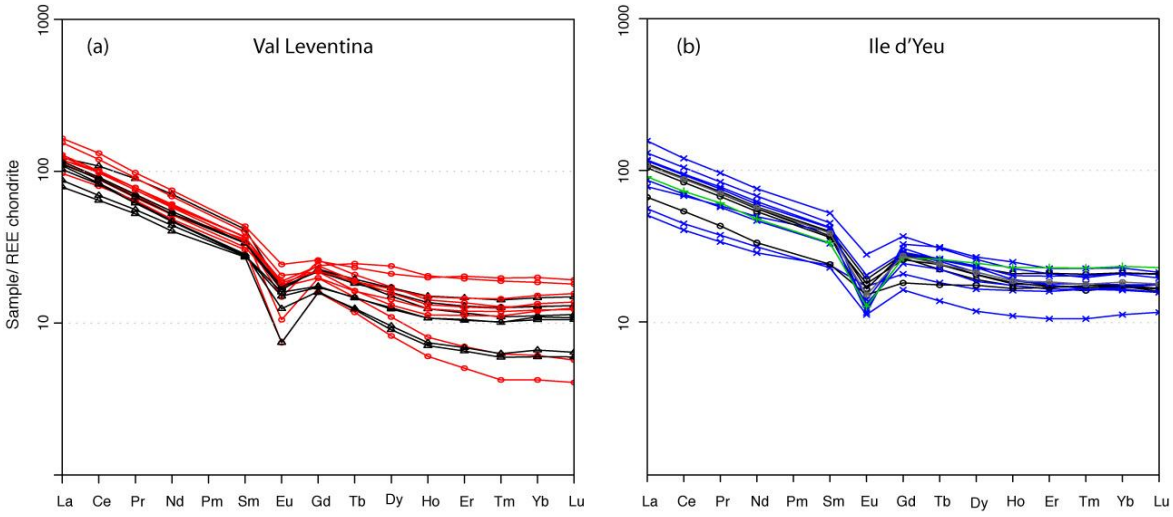


Fig. 5 : Chondrite-normalized (Boynton 1984) REE patterns of the granitoid orthogneisses (black) and Mg-rich shear zone rocks (red and blue) from (a) Val Leventina and (b) Ile d'Yeu. The similarities between the patterns of the shear zones and the orthogneisses and between the two distant localities are striking.

We expect that this project will be a base for a larger integrated study at the scale of the Alps and Western Carpathians in collaboration with our Czech, Slovak and Swiss colleagues. This collaboration already started and is materialised by the joint sampling campaigns in the Alps and Western Carpathians in 2009 and 2010. The goal would be a comparative study of the different types of localisation of rocks affected by Mg-metasomatism (whiteschists, leucophyllites, magnesites, talc-schists and associated Mg-micaschists,…).

References

Boynton, W. V., 1984. Cosmochemistry of the rare earth elements: meteorite studies. In: *Rare Earth Element Geochemistry* (ed Henderson, P.), pp. 63-114, Elsevier, Amsterdam.

Challandes N., Marquer D. &Villa I. M. (2008) PTt modelling, fluid circulation, and 39Ar-40Ar and Rb-Sr mica ages in the Aar Massif shear zones (Swiss Alps). *Swiss J. Geosci*., 101, 269-288, DOI 10.1007/s00015-008-1260-6.

Chopin, C., Henry, C. & Michard, A., 1991. Geology and petrology of the coesite-bearing terrain, Dora Maira massif, Western Alps. *European Journal of Mineralogy*, **3**, 263-291.

Compagnoni, R. & Hirajima, T., 2001. Superzoned garnets in the coesite-bearing Brossasco-Isasca Unit, Dora-Maira massif, Western Alps, and the origin of the whiteschists. *Lithos*, **57**(4), 219-236.

Demény, A., Sharp, Z. D. & Pfeifer, H.-R., 1997. Mg-metasomatism and formation conditions of Mg-chlorite-muscovite-quartzphyllites (leucophyllites) of the Eastern Alps (W. Hungary) and their relations to Alpine whiteschists. *Contributions to Mineralogy and Petrology*, **128**(2), 247-260.

Donguy, P.-A., 2008. Dater la déformation varisque : exemples des zones de cisaillement métasomatiques de l'Ile d'Yeu. *Unpub. MSc Thesis, Université Rennes 1, Rennes.*

Ferraris, C., Chopin, C. & Wessicken, R., 2000. Nano- to micro-scale decompression products in ultrahigh-pressure phengite: HRTEM and AEM study, and some petrological implications. *Am. Mineral.*, **85**, 1195-1201.

Galley, A. G., Hannington, M. D. & Jonasson, I. R., 2007a. Volcanogenic massive sulphide deposits. In: *Mineral Deposits of Canada: A Synthesis of Major Deposit Types, District Metallogeny, the Evolution of Geological Provinces, and Exploration Methods* (ed Goodfellow, W. D.) *Geological Association of Canada, Mineral Deposits Division, Special Publications*, **5**, pp. 141-161, Geological Association of Canada.

Galley, A. G., Syme, E. C. & Bailes, A. H., 2007b. Metallogeny of the Paleoproterozoic Flin Flon Belt, Manitoba and Saskatchewan. In: *Mineral Deposits of Canada: A Synthesis of Major Deposit Type…* (ed Goodfellow, W. D.) *Geological Association of Canada, Mineral Deposits Division, Special Publications*, **5**, pp. 509-531, Geological Association of Canada.

Korzhinskii, D. S., 1959. *Physicochemical Basis of the Analysis of the Paragenesis of Minerals*. Consultants Bureau, New York, 142 pp.

Kosler, J., 2007. Laser ablation ICP-MS - a new dating tool in Earth science. *Proceedings of the Geologists Association*, **118**, 19-24.

Kováčik, M., 1996. Kyanite-magnesian chlorite schist and its petrogenetic significance (the Sinec Massif, southern Veporic Unit, Western Carpathians). *Geologica Carpathica*, **47**, 245-255.

Marquer, D. & Burkhard, M., 1992. Fluid circulation, progressive deformation and chemical mass-transfer in the upper crust: example of basement-cover relationships in the external cristalline massifs (Switzerland). *Journal of Structural Geology*, **14**(8/9), 1047-1058.

Marquer, D., Petrucci, E. & Iacumin, P., 1994. Fluid advection in shear zones: evidence from geological and geochemical relationships in the Aiguilles Rouges Massif (Western Alps - Switzerland). *Schweizerische Mineralogische und Petrographische Mitteilungen*, **74**(1), 137-148.

Mernagh, T. P., Wyborn, L. A. I. & Jagodzinski, E. A., 1998. 'Unconformity-related' U±Au±platinum-group-element deposits. *AGSO Journal of Australian Geology and Geophysics*, **17**(4), 197-205.

Moine, B., Fortuné, J. P., Moreau, P. & Viguier, F., 1989. Comparative mineralogy, geochemistry, and conditions of formation of two metasomatic talc and chlorite deposits; Trimouns (Pyrenees, France) and Rabenwald (Eastern Alps, Austria). *Economic Geology*, **84**(5), 1398-1416.

Nemeth, Z., Prochaska, W., Radvanec, M., Kováčik, M., Madaras, J., Koděra, P. & Hrasko, L., 2004. Magnesite and talc origin in the sequence of geodynamic events in Veporicum, Inner Western Carpathians, Slovakia. *Acta Petrologica Sinica*, **20**(4), 837-854.

Oliot, E., Goncalves, P. & Marquer, D., 2010. Role of plagioclase and reaction softening in a metagranite shear zone at mid-crustal conditions (Gotthard Massif, Swiss Central Alps). *Journal of Metamorphic Geology*, **28**, 849-871.

Pawlig, S. & Baumgartner, L. P., 2001. Geochemistry of a talc-kyanite-chloritoid shear zone within the Monte Rosa granite, Val d'Ayas, Italy. *Schweizerische mineral. und petrographische Mitteilungen*, **81**(3), 329-346.

Pelleter, E., Cheilletz, A., Gasquet, D. et al., 2007. Hydrothermal zircons: A tool for ion microprobe U-Pb dating of gold mineralization (Tamlalt-Menhouhou gold deposit - Morocco). *Chemical Geology*, **245**(3-4), 135-161.

Philippot, P., Chevallier, P., Chopin, C. & Dubessy, J., 1995. Fluid composition and evolution in coesite-bearing rocks (Dora-Maira massif, Western Alps): implications for element recycling during subduction. *Contributions to Mineralogy and Petrology*, **121**(1), 29-44.

Pitra, P. & Antonoff, V., 2007. Metamorphic conditions of the Variscan collision inferred from metasomatic shear zones (Ile d'Yeu, Armorican Massif, France). *Mechanics of Variscan Orogeny: a modern view on orogenic research (September 13-15 2007), Orléans, France*

Pitra, P., Boulvais, P., Antonoff, V. & Diot, H., 2008. Wagnerite in a cordierite-gedrite gneiss: Witness of long-term fluid-rock interaction in the continental crust (Ile d'Yeu, Armorican Massif, France). *American Mineralogist*, **93**, 315-326.

Pitra, P., Kouamelan, A.N., Ballèvre, M., & Peucat, J.J., 2010. Palaeoproterozoic high-pressure granulite overprint of the Archaean continental crust: evidence for homogeneous crustal thickening (Man Rise, Ivory Coast). *Journal of Metamorphic Geology*, **28**, 41-58.

Robb, L., 2005. *Introduction to ore-forming proceses*. Blackwell Publishing, Oxford.

Rossi, M., 2005. Déformation, transferts de matière et de fluide dans la croûte continentale: application aux massifs cristallins externes des Alpes, *Université Joseph Fourier - Grenoble 1, Grenoble*.

Rouhunkoski, P., 1968. On the geology and geochemistry of the Vihanti zinc ore deposit. *Bulletin de la Commission Géologique de Finlande*, **236**, 1-121.

Schaltegger, U., Pettke, T., Audetat, A. et al., 2005. Magmatic-to-hydrothermal crystallization in the W-Sn mineralized Mole Granite (NSW, Australia): Part I: Crystallization of zircon and REE-phosphates over three million years - a geochemical and U-Pb geochronological study. *Chemical Geology*, **220**(3-4), 215-235.

Schertl, H.-P. & Schreyer, W., 2008. Geochemistry of coesite-bearing ''pyrope quartzite'' and related rocks from the Dora-Maira Massif, Western Alps. *European Journal of Mineralogy*, **20**, 791–809.

Schreyer, W., 1977. Whiteschists: Their compositions and pressure-temperature regimes based on experimental, field, and petrographic evidence. *Tectonophysics*, **43**(1-2), 127-144.

White, R. W., Powell, R. & Baldwin, J. A., 2008. Calculated phase equilibria involving chemical potentials to investigate the textural evolution of metamorphic rocks. *Journal of Metamorphic Geology*, **26**(2), 181-198.

Inverted metamorphic sequences

Extended abstract of an ANR project, submitted in 2011 (leader – Michel Ballèvre).

Mechanisms of heat transfer in a thickened crust: the inverted metamorphism in the Variscan belt

Inverted metamorphic zonings develop in orogens dominated by continental collision and record their thermo-mechanical evolution. The main goal of this project is to understand their formation and preservation. Indeed, in zones of lithospheric convergence, crustal-scale thrusts lead to the thickening of the continental crust and are commonly associated with local inversions of the apparent metamorphic gradient. We aim to understand
1) whether, and to what extent does this inversion reflect the inversion of the geothermal gradient
2) how can this inversion be preserved along strike of some mountain belts (over 3000 km in the case of the Himalayan and Variscan orogen).

In order to answer these questions, our project combines in a complementary way detailed case studies and numerical modelling.

The chosen **case study** is the European Variscan belt, where inverted metamorphic sequences are observed from the NW part of Spain till the Bohemian massif. The inverted metamorphism has mostly been studied in the Himalayas, without yielding a consensual answer to the above questions. Then the Variscan belt represents an opportunity to study another case, with a different history, but similar scale. The comparison of the two belts will allow to abstract from the specificities of each orogen and retrieve the fundamental parameters, which control the development of the common phenomenon (inverted metamorphic zoning).

We propose to study in detail an example, the existence of which was recently shown by our team (Pitra et al., 2010) – the Champtoceaux Complex in the French Armorican Massif. We shall also explore a secondary target, the Lot valley in the southern Massif Central, from which preliminary results have been obtained some 25 years ago (Burg et al., 1984, 1986).

Our first objective, of **petrological** character, is to establish (1) the initial dip of the original subduction zone at the scale of the orogen, by confirming the existence of a pressure gradient among the eclogite lenses scattered below the major thrust zone, and (2) the P–T paths of the rocks across the inverted gradient. This will test the presence or absence of discontinuities within the inverted sequence and the possible superposition of several P–T cycles.

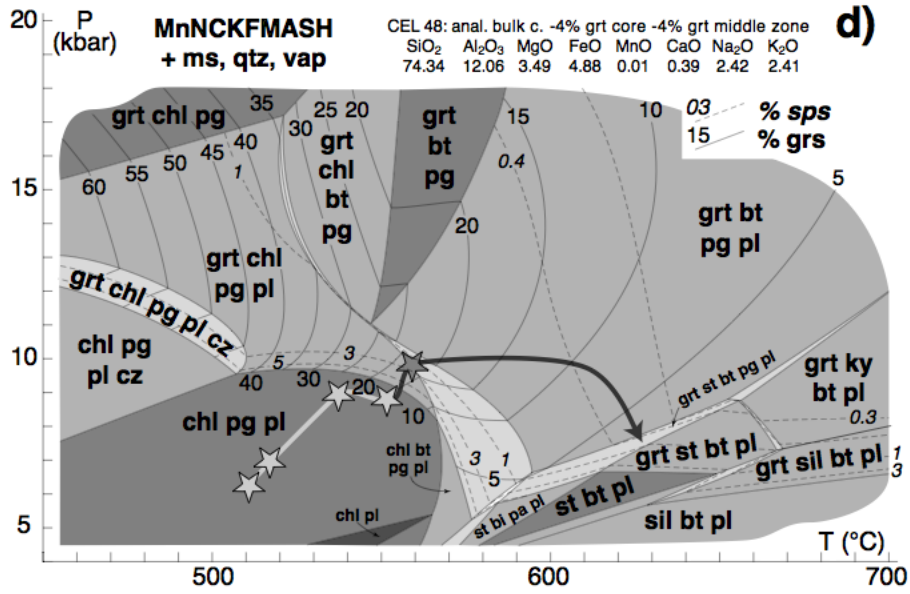
Our second objective, of **geochronological** character, aims to establish the age of the eclogite-forming episode, still subject to uncertainties, and to clarify the age of the post-eclogite partial melting, recorded in the upper unit. Finally, the cooling history of the nappe stack will be examined in detail, in order to understand if the recorded interval of ages reflects different closure mechanisms of the isotopic systems in different samples, a diachronous uplift of the different stacked units, or other factors.

The goal of the **numerical modelling** will be to address the problem of the formation and preservation of an inverted metamorphic sequence through parametric studies. The latter will aim to quantify the physical key parameters such as the rate of thrusting, thermal conductivity of the rocks, influence of shear-heating, etc. For this, modelling will be performed at various degrees of complexity. First, kinematically-controlled thermal models, in order to access the

likely range of values of the parameters that allow the development of an inverted metamorphic sequence. Then coupled thermo-mechanical models, taking into account phase transformations and erosional processes, in order to understand the possible interactions between these parameters. This part of the project will be closely related to the petrological and geochronological studies that will yield detailed pressure – temperature – time data, indispensable to finely constrain the models.

P-T paths

Estimations of peak temperatures have been done by Pitra et al. (2010). However, studies in the Himalayan belt have shown that P-T paths leading to similar peak T conditions can be quite different on both side of the crustal-scale thrust associated to the inverted metamorphism, thus recording major differences in terms of thermal perturbations in the thickened crust. P-T paths for individual rock samples will be calculated in the Champtoceaux Complex and used to answer the following key questions, namely (i) whether the P-T paths are all similar or not across the inverted gradient; (ii) if some units record a single P-T loop, or more complex shapes (like a P increase at some stage during their exhumation, as expected in some models for the inverted metamorphism).
We shall study the fine-scale zoning of the garnet grains, and the associated evolution of the chemistry of the other phases, in order to detect the smallest departures of the P-T paths that could be associated to the inverted metamorphism. Preliminary results calculated by P. Pitra on one sample with strongly zoned garnets show the feasibility of such an approach:



Interpretation of the garnet zoning in terms of P-T evolution using a calculated pseudosection. This preliminary result is particularly encouraging and demonstrates the feasibility of our study.

References

Burg, J.-P., Leyreloup, A.F., Marchand, J., and Matte, P. (1984) Inverted metamorphic zonation and large-scale thrusting in the Variscan Belt: an example in the French Massif Central, p. 47-61. Geological Soc. Special Pub., 14.

Burg, J.-P., Delor, C.P., Leyreloup, A.F., and Romney, F. (1986) Inverted metamorphic zonation and Variscan thrust tectonics in the Rouergue area (Massif Central, France), p. 423-439. Geological Soc. Special Pub., 43.

Pitra, P., Ballèvre, M., and Ruffet, G. (2010) Inverted metamorphic field gradient towards a Variscan suture zone (Champtoceaux Complex, Armorican Massif, France). Journal of Metamorphic Geology, 28(2), 183-208.

Statistical methods

The goal of the study of metamorphic rocks is in general to determine the evolution of the physico-chemcial conditions (pressure-temperature-composition) in time, in order to set them in a geodynamic context. This information is therefore the basis for all tectonic interpretations and models. Yet, this information is subject to **uncertainty**, the importance of which is systematically neglected or underestimated. This uncertainty concerns not only the absolute value of the pressure–temperature conditions, but also the character of their evolution in time (the form of the "P–T paths"). It comes from several sources:

- **"geological"** uncertainty, related to the problem of understanding correctly the rocks – estimating the equilibration volumes, interpreting the equilibrium assemblages, the heterogeneity of mineral compositions, etc.
- **analytical** uncertainty,
- **thermodynamic** uncertainty, associated with the fundamental thermodynamic data and the formulation of the mixing models for solution phases.

Realistic estimation of these uncertainties and their **propagation** through the thermodynamic calculations allows to get results that approach the reality, and to have a better idea of their reliability. The information on the reliability of the petrological data (P and T at a given moment, reflecting the transient geotherm; their evolution in time, reflecting e.g. a decompression accompanied by heating, or cooling, etc.) can appear crucial, since they are used as the base for elaborating or justifying numerous **tectonic models** (e.g. on the exhumation of rocks in subduction zones, the formation of mountain belts, etc.) and underestimating the uncertainties may lead to unjustified invalidation of some of the models.

In the framework of my research, this aspect is crucial, for example, in the interpretation of the development of the **inverted metamorphic sequences**. Indeed, this interpretation depends on how the petrological record (in particular e.g. the chemical zoning of minerals) can be interpreted in terms of depth and temperature variations (related for example to the transient overload due to the emplacement of a nappe) and the precision, with which this can be done. But it plays an important role also in the estimation of the pressure – temperature conditions, and hence the geothermal gradients, in **subduction zones**.

In order to approach this aspect that I believe fundamental for the future of metamorphic petrology, I spent four weeks with Roger Powell at the University of Melbourne, Australia. I would like to further develop this aspect by acquiring the necessary mathematical tools and applying them to the various running projects.

C – Annexes